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RENDICONTI DEL CONVEGNO
DI
FISICA DEI SOLIDI E DEI LIQUIDI

TENUTOSI NELLA VILLA MONASTERO A VARENNA
DAL 5 AL 7 GIUGNO 1954

INDICE GENERALE

PRESENTAZIONE

DI

G. POLVANI

Presidente della Società Italiana di Fisica

Per iniziativa del prof. LUIGI GIULOTTO dell'Università di Pavia e dei professori GIORGIO CARERI dell'Università di Roma e FAUSTO FUMI della Università di Milano, l'altr'anno, nei giorni 5, 6, 7 Giugno, ebbe luogo a Varenna, nella Villa Monastero, messa gentilmente a disposizione dall'Ente Villa Monastero, un Convegno, assai ristretto, organizzato dallo stesso prof. GIULOTTO, di cultori, stranieri e italiani, di studi della Fisica dello stato solido e dello stato liquido.

Gli argomenti trattati e le persone che più vivamente presero parte al Convegno, risultano chiaramente dall'indice preposto a questi *Rendiconti*, ai quali la Direzione del giornale *Il Nuovo Cimento* di buon grado dedica questo fascicolo.

A proposito di questo Convegno, il Consiglio di Società desidera esprimere il suo plauso sia a chi ne ha avuto l'iniziativa sia a chi lo ha attuato: e ciò perchè, anzitutto, il Convegno stesso ha ulteriormente promosso in Italia gli studi di Fisica dello stato condensato; e poi perchè esso è stato il germe di una più ampia iniziativa che si attuerà negli anni prossimi, con Corsi internazionali, che verranno tenuti a Villa Monastero, su alcuni particolari aspetti della Fisica dei solidi e dei liquidi.

Qui, licenziando il fascicolo, la Direzione desidera porgere ai professori GIULOTTO, CARERI e FUMI e ai dottori GIOVANNI BOATO, GIANFRANCO CHIAROTTI e ROBERTO FIESCHI il suo ringraziamento per la collaborazione data nel preparare per la stampa questi *Rendiconti*.

PARTE PRIMA

Fisica dei solidi.

Physical Properties of the Alkali Halide Crystals (*).

F. SEITZ

University of Illinois - Urbana, Ill. (U.S.A.)

1. – Introduction.

The study of the physical properties of alkali halide crystals has assumed an almost unique position in the field of Solid State Physics, rivalled only by the research centering about the semi-conductors which have the diamond structure. The work on the alkali halides is made particularly remarkable by the fact that the stimulus has arisen from fundamental curiosity rather than from immediate applicational work. Nevertheless, it has had far-reaching pratical consequences because many of the most valuable concepts and tools of solid state science have developed as a result of investigations in the field.

The present paper is devoted to a brief survey of the problems which seem to offer the most fruitful source for future investigations. A far more detailed summary of the research carried out in the past may be found in a review article (1) prepared recently by the writer.

2. – Imperfections in Clear Crystals.

At the present time, we possess a fairly clear insight into the nature of the point lattice defects which occur in clear uncolored alkali halide crystals. A host of investigations, based upon the measurement of electrolytic conductivity and density, leave little doubt that the disorder is of the Schottky type, consisting of equal numbers of positive- and negative-ion vacancies. The

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(*) The writer is deeply indebted to The Office of Scientific Research of ARDC-USAF for assistance in travel.

(1) F. SEITZ: *Rev. Mod. Phys.*, 26, 7 (1954).

relative numbers of the two types of imperfection can be altered by adding halides of divalent metals within the range of the solubility limits, for each divalent ion is accompanied by a positive-ion vacancy. Research based on this fact has made it possible to determine the actual concentrations of Schottky defects in perfect crystals to relatively high precision.

Closely connected with the problem of determining the nature and density of the lattice defects is that of determining the degree of association of oppositely charged vacancies and of the divalent ions and their compensating positive-ion vacancies. Measurements of the electrolytic conductivity of Alkali Halides containing divalent additions as a function of temperature and composition in the range of temperature where the impurities have a major influence (impurity range) provide some critical information on this issue, as we shall see below. Theoretical aspects of this problem have been investigated in detail by LIDIARD ([2]) in recent years. In particular he applied a modified version of the Debye-Hückel theory of electrolytes to the alkali halides. Still further BASSANI and FUMI ([3]) have made detailed calculations of the energy of interaction of equilibrium defects in the Alkali Halides with the use of the Born theory of ionic crystals, extending earlier work of REITZ and GAMMEL ([3]).

MAPOTHER, CROOKS and MAURER ([4]) have demonstrated experimentally that the Einstein relation connecting the conductivity and diffusion coefficient associated with a given ion need not be valid in the impurity range of electrolytic conductivity in the Alkali Halides. ASCHNER ([5]) has extended measurements of this type in sodium and potassium chloride under conditions in which the amount of divalent addition is carefully controlled. He has found that the Einstein relation is always obeyed to within experimental error in the intrinsic range of conductivity, that is, in the range where the density of thermally induced Schottky defects is so great that the influence of impurities is negligible. The deviations found in the impurity range depend upon the amount of foreign additions as well as upon the added agent. In the simplest case studied, namely that centering about the addition of cadmium chloride to sodium chloride, the ratio of the measured diffusion coefficient to that computed from the ionic conductivity varies more or less linearly with the concentration of cadmium. This behavior is what one might expect if the fraction of cadmium ions having positive-ion vacancies closely associated with

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([2]) A. B. LIDIARD: *Phys. Rev.*, **94**, 29 (1954).

([3]) J. R. REITZ and J. L. GAMMEL: *J. Chem. Phys.*, **19**, 894 (1951); F. BASSANI and F. G. FUMI: *Phil. Mag.*, **45**, 228 (1954); *Nuovo Cimento*, **11**, 274 (1954). Further calculations by BASSANI and FUMI are reported in the Proceedings of this conference. (see p. 114).

([4]) D. E. MAPOTHER, H. N. CROOKS and R. J. MAURER: *J. Chem. Phys.*, **18**, 1231 (1950).

([5]) J. F. ASCHNER: *Thesis*, University of Illinois, 1954.

them is proportional to the concentration of cadmium. The same results, when analyzed with use of Lidiard's theory of association, appear to reveal the effects of association unambiguously. It seems highly desirable to extend measurements of this type to a wider family of foreign additions. In particular, it would be interesting to obtain a number of empirical association energies to compare with the calculated values of BASSANI and FUMI.

One of the interesting by-products of the existence of association forces between foreign ions and vacancies is the fact that foreign ions may diffuse more rapidly in the crystal than the parent ions because they have vacancies nearby for a larger fraction of the time. This effect was first detected by ETZEL and MAURER in sodium chloride containing cadmium ions. It has been investigated more extensively in recent research by CHEMLA (6). There seems to be little doubt that association has a profound effect upon the rate of diffusion of foreign atoms which have a strong affinity for Schottky defects.

It is also interesting to note that ASCHNER found that the fractional deviation between the measured diffusion coefficient and that derived from the Einstein relation with the electrolytic conductivity in the impurity range actually is larger in some of the purest crystals than in some of those intentionally contaminated with cadmium. The results seem to imply that an unknown impurity present in the purest crystals he studied has a substantially larger effect per added ion in influencing the diffusion coefficient than the divalent ions normally used in such studies.

Our understanding of the nature of the imperfections in clear Alkali Halide crystals has been advanced extensively by calculations of the energies of various dislocations in sodium chloride by APKER, HUNTINGTON and THOMSON (7). These investigators have combined calculations dealing with the long range elastic strain and the short range non-Hookian strain. Among other things they have found that screw dislocations have a substantially lower energy than edge dislocations, so that one would expect well annealed crystals to contain screw dislocations primarily. Similar conclusions seem to be valid for the silver halides and may well explain why well-annealed silver halide crystals are not photosensitive. The calculations still leave unsettled many basic questions such as those dealing with a tendency for a slip to occur preferentially on (110) planes in the alkali halides.

It should be emphasized that we still lack reconfirmation of the old exper-

(6) M. CHEMLA: *Thesis*, University of Paris (1954). The writer is indebted to Professor CHEMLA for the opportunity of reading a copy of the thesis prior to publication.

(7) J. D. APKER, H. B. HUNTINGTON and R. THOMSON (as yet unpublished work). The writer is indebted to these investigators for the opportunity of discussing their preliminary results.

iments of GYULAI and HARTLY and STEPANOW (8) on the change of electrolytic conductivity accompanying cold work. This research, which seems to give striking evidence that moving dislocations generate positive- and negative-ion vacancies, has not yet been duplicated on a scale which gives one complete confidence in the interpretation proposed by the writer. As we shall see below there are somewhat indirect experiments, carried out by KÄNZIG and UETA (9), which appear to have important bearing on the experiments of GYULAI and HARTLY.

3. – *F* Centers.

The model of the *F* center which was first proposed by DE BOER (10) on the basis of the experiments carried out principally at Göttingen, namely that the center consists of an electron bound to a halogen-ion vacancy, has remained an anchor point in our understanding of the properties of the colored Alkali Halides. Moreover, there is good reason to believe that the most prominent bands which can be observed in the visible and near infra-red regions of X-rayed or additively colored Alkali Halides, that is, the F, F', R and M bands, are to be associated with isolated and coagulated (11) *F* centers. All investigations seem to confirm the general picture of coagulation proposed by the writer in 1946. Among the most striking new observations dealing with *F*-centers are those (12) of HUTCHINSON and NOBLE and of KIP, KITTEL, and their co-workers on the spin resonance found in colored Alkali Halides.

As mentioned previously, KÄNZIG and UETA (9) have carried out extensions of the study of additively colored crystals which seem to have an important bearing on the generation of vacancies during plastic flow. They have examined the bleaching of the *F* band in additively colored crystals of NaCl when the latter are irradiated with light near the center of the band. The most significant bleaching process in these experiments occurs as a result of the transfer of electrons from isolated *F* centers to aggregates. This process is accompanied by the development of the *R* and *M* bands. The investigators have found that the efficiency of the conversion from the *F* band to the *M* and *R* bands is greatly increased after the crystal has been deformed. The conversion is

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(8) Z. GUYLAI and D. HARTLY: *Zeits. f. Phys.*, **51**, 378 (1928); Z. GYULAI: *Zeits. f. Phys.*, **78**, 630 (1932); A. W. STEPANOW: *Zeits. f. Phys.*, **81**, 560 (1933).

(9) M. UETA and W. KANZIG: *Phys. Rev.*, **944**, 1390 (1954).

(10) J. H. DE BOER: *Rec. trav. chim. Pays-Bas*, **56**, 301 (1937).

(11) F. SEITZ: op. cit., *Rev. Mod. Phys.*, **18**, 384 (1946).

(12) C. A. HUTCHINSON: *Phys. Rev.*, **75**, 1769 (1949); C. A. HUTCHINSON and G. A. NOBLE: *Phys. Rev.*, **87**, 1125 (1952); M. TINKHAM and A. F. KIP: *Phys. Rev.*, **83**, 657 (1951); A. H. KAHN and C. KITTEL: *Phys. Rev.*, **89**, 315 (1953), *et qse.*.

particularly great when the crystals are deformed and bleached at room temperature. In fact the F band could be almost obliterated. The effect is much smaller if the crystals are deformed and bleached at liquid nitrogen temperatures. Moreover, the F'band rather than the R and M bands appears under these conditions. However, the crystals deformed at low temperatures bleach in essentially the same way as those deformed at room temperature if they are warmed to room temperature subsequent to plastic flow at low temperatures and are irradiated there.

The results of the experiments would seem to be easy to interpret if one postulates that Schottky defects are generated as a result of plastic flow. The extra defects, in particular the positive-ion vacancies and the pairs of positive- and negative-ion vacancies, presumably are mobile at room temperature and can participate in the formation of aggregates. Unfortunately, the experiments seem to shed little light on the question of whether the vacancies formed by cold work are relatively isolated from one another or whether they are ordered in arrays which dissolve when the crystals are near room temperature.

4. – The V Bands.

MOLLWO's observations [13] on the absorption bands observed in alkali halides containing a stoichiometric excess of halogen demonstrated clearly that one might expect a family of centers which absorb light in the ultra violet and which are antimorphic to F-type centers. Presumably holes and positive-ion vacancies play the role of electrons and negative-ion vacancies in the new centers. At the present time almost all the information we possess on the nature of the V bands associated with the centers, is derived from the study of crystals darkened by ionizing radiations. Thus F-type bands are present along with the V bands. Nevertheless, it has proved possible to unravel a few of the characteristic properties of the centers responsible for the V bands. Such work suggests that the V centers are, if anything, considerably more intricate than the F centers.

The simplest of the V centers appears to be that designated as V_1. The V_1 absorption band, associated with it, was first discovered by CASLER, PRINGSHEIM and YUSTER [14] on specimens of KCl irradiated at liquid nitrogen temperature. The band is fugitive in the sense that it bleaches when the crystal is warmed to room temperature. The rate of bleaching becomes rapid

(13) E. MOLLWO: *Nachr. Akad. Wiss. Göttingen*, **1935**, 215; *Ann. der Phys.*, **29**, 394 (1937).

(14) R. CASLER, P. PRINGSHEIM and P. YUSTER: *J. Chem. Phys.*, **18**, 887, 1564 (1950).

when the temperature reaches -135 °C. The existing evidence makes it reasonable to assume that the V_1 center is the antimorph of the simple F center, consisting of a hole bound to a positive-ion vacancy. In addition to it, there are at least three other V centers which appear to be associated with aggregates formed of positive-ion vacancies and holes.

Dutton, Maurer, Teegarden [15] have carried out a series of experiments concerning the stability of the V_1 center using specimens of KCl colored by X-irradiation. Dutton and Maurer have found that the crystals become conducting when the V_1 band bleaches during warming of the specimen from liquid nitrogen temperature. Experiments suggest that the conductivity is to be ascribed to the migration of holes which are freed from positive-ion vacancies and wander about until they are captured by other centers. The results indicate that the activation energy required to free a hole from a V_1 center as a result of thermal fluctuations is of the order of a few tenths of a volt, in contrast with the energy of the ultraviolet light quantum required to excite the V_1 center from its ground state to the first excited state.

Casler, Pringsheim and Yuster noted that the V_1 center could be bleached with light absorbed in the V_1 band. Maurer and Teegarden have found that such bleaching does not seem to engender an appreciable photocurrent. Presumably the excited hole tunnels to another center where it may become trapped or may recombine with an electron. The displacement of charge is insufficient to give an appreciable current. There is a prominent F' band present if the crystals are darkened at liquid nitrogen temperature. This band decreases very strongly when the V_1 band is bleached with light absorbed in the band. The F band remains relatively unchanged at first. Essentially the same result is found if the crystal is darkened at liquid nitrogen temperature (83 °K) and is bleached with light at 35 °K. In this case however, a part of the V_1 band is transformed into the H band, first observed by Duerig and Markham [16]. The writer has suggested that the H band arises from a center consisting of a hole attached to a pair of vacancies of opposite sign, a unit which is not stable at liquid nitrogen temperatures. In any case, the experiments suggest that some of the holes tunnel to F' centers and others tunnel to paired vacancies forming H centers when the crystal darkened at liquid nitrogen temperature is irradiated with light in the V_1 band at 35 °K.

The intensity of the F' band is very low when crystals of KCl are darkened with X-rays at 35 °K. If crystals treated in this way are irradiated with light in the V_1 band, the band is converted in the main to the H band, the F band decreasing only slightly.

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(15) D. Dutton and R. J. Maurer: *Phys. Rev.*, **90**, 126 (1953); K. Teegarden and R. J. Maurer (to be published).

(16) W. H. Duerig and J. J. Markham: *Phys. Rev.*, **88**, 500 (1952) *et seq.*

Attention should be called to one as yet unresolved aspect of the work of DUTTON and TEEGARDEN. DUTTON observed that the F band is bleached preferentially when the V_1 centers are bleached by warming from liquid nitrogen temperature. The F' band is relatively unaffected when the temperature of the specimen passes through the range near $-135\,^{\circ}$C where the V_1 band decreases most rapidly. Instead the F' band bleaches independently at a somewhat higher temperature. TEEGARDEN studied the thermal bleaching of specimens which had been darkened at 35 °K and in which the F' band consequently was almost absent. He found that they have almost the same behavior as DUTTON's specimens. All this indicates that the F' band plays an almost negligible role when V_1 centers are bleached through warming. In contrast, the F' band is bleached in preference to the F band when V_1 centers are destroyed by light quanta.

It is perhaps not difficult to understand why the holes associated with excited V_1 centers should tunnel preferentially to electrons attached to F' centers, for such electrons are distributed over a larger volume than the electrons attached to F centers. On the other hand it is not easy to see why the holes released during warming seemingly prefer to recombine with F centers.

It should be mentioned that the low photoconductivity observed during bleaching of the V_1 band with light is not characteristic of all of the V bands. MAURER and TEEGARDEN have found that another band, termed V_4, can act as the seat of an appreciable photocurrent which presumably is the result of the freeing of holes from a complex unit.

It would appear almost imperative that research be carried out on additively colored crystals containing a stoichiometric excess of halogen. It seems very difficult to circumvent the influence of the F-type centers on the V centers in specimens darkened by ionizing radiation.

5. – Color Centers in Crystals Containing Additions.

As our knowledge of the properties of pure colored crystals and of uncolored crystals containing foreign additions increases, it becomes evident that much can be expected from the study of the properties of colored crystals containing foreign additions. This field has by no means been neglected, for there has been substantial work on the properties of the alkali halides containing alkali metal hydrides (U centers) and on the coloration which can be induced in crystals containing controlled amounts of the halides of divalent metals. Although the latter type of study was initiated before the war by PICK (17) it has been pursued since with appropriate vigor only by Italian

(17) H. PICK: *Ann. der Phys.*, **35**, 73 (1939); *Zeits. f. Phys.*, **114**, 127 (1939); F. SEITZ: *Phys. Rev.*, **83**, 134 (1951).

investigators, CAMAGNI, CHIAROTTI, FUMI and GIULOTTO [18]. Since this work is being reported independently at the Varenna Conference there is no need for further elaboration here. It is appropriate to say, however, that the research represents an exceedingly important addition to the very profitable work in the field and may well open one of the richest chapters in the subject.

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[18] P. CAMAGNI, G. CHIAROTTI, F. G. FUMI and L. GIULOTTO: *Phil. Mag.*, **45**, 225 (1954); P. CAMAGNI and G. CHIAROTTI: *Nuovo Cimento*, **11**, 1 (1954); G. CHIAROTTI, F. G. FUMI and L. GIULOTTO: *Proceedings of the Bristol Conference on Lattice Defects in Solids* (July 13-17, 1954).

INTERVENTI E DISCUSSIONI

— F. G. FUMI:

I wonder if you would care to comment on the non-linearity of the conductivity-temperature plots in the low temperature region. One may attribute this non-linearity to the change in vacancy association at these temperatures. The slope would then not be given simply by the activation energy for migration.

— F. SEITZ:

I quite agree that the curvature of the conductivity-temperature plots is a real feature and that it can be explained at least qualitatively in the way you suggest. ASCHNER, in his measurements on Cd doped NaCl crystals, found definite non-linearity. He also found that by heating the crystals for a certain time at 700 °C the ionic conductivity in the low temperature region was enhanced, suggesting that some breakage of vacancy agglomerates had occurred.

F. G. FUMI:

I would like to hear your opinion on the evidence regarding vacancy pairs. One would expect evidence for the role of vacancy pairs in ionic crystals from measurements of ionic conductivity and diffusion coefficients in the intrinsic range: there should be deviation from the Einstein relation. Furthermore in the temperature interval in which vacancy pairs are the important carriers, one would expect equal mobility for the two ionic species of the crystals. Neither of these facts seems to be verified by experiments.

— F. SEITZ:

WITT (Göttingen) found deviations from the Einstein relations in the intrinsic range in KCl. However, a systematic deviation must have crept into his measurements on diffusion of K in KCl, probably owing to the weak radioactivity of his samples. ASCHNER at Urbana has found no such deviation within the accuracy of his measurements (15%). There is some evidence on the existence of pairs of more direct nature: for instance DELBECQ (Argonne, Chicago) has found that thin layers of alkali halides deposited on a KCl crystal subjected to X-irradiation become amorphous if the tem-

perature of irradiation is above $-135\,°C$ while they do not if the temperature is below $-135\,°C$. I interpret these measurements to imply that a lattice entity (the pair) becomes mobile at about that temperature.

— G. CHIAROTTI:

An experiment which may confirm the existence of vacancy agglomerates in alkali halide crystals is the following. We bleach part of the F band of a crystal darkened by X-rays and determine the quantum yield of bleaching. After a few hours we resume the bleaching: if during this time the vacancies which had been freed by the bleaching have agglomerated the quantum yield for bleaching should now be greater. Preliminary measurements performed at Pavia appear to confirm this.

— A. B. SCOTT:

We have performed at Oregon State some experiments on photoconductivity of additively coloured alkali halide crystals and found that the photoconductance dropped much more than the optical absorption on illuminating in the F band. We interpret these measurements to imply a decrease in the range of photoelectrons. I wonder if anybody is attempting to study the effects of cold work on photoconductance in relation to the vacancy production by dislocations.

— F. SEITZ:

I am not aware of any such work being carried out. However, INCHAUSPÉ has started at Urbana some work on photoconductivity. He has confirmed for instance the old SMAKULA result that non-coloured crystals do not show photoconductivity when illuminated in the tail of the absorption band.

— P. G. BORDONI:

I wonder if anybody has attempted to establish a correlation between mechanical and optical properties in alkali halide crystals.

— F. SEITZ:

FRANKL and READ have recently published a paper showing that the internal friction in alkali halide crystals is decreased by darkening. They think that dislocations are pinned down by vacancy clusters. KÄNZIG and UETA have also found that the F band bleaches more easily in cold-worked crystals. There is then the classical work by PRZIBRAM and coworkers which shows that plastic deformation increases the darkenability of a crystal.

Color Center Reactions.

A. B. SCOTT

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In the reactions which color centers undergo in the alkali halides we have an interesting set of processes, both thermal and photochemical, which is somewhat unique among reactions occurring in the solid state. The solvent, or host-lattice, is transparent in the visible; the solute, that is, the color centers and their associated products and progenitors, is, by usual standards, very dilute. The transparency of the solvent is of the greatest convenience as not only can the course of reactions be followed by colorimetric methods, but many processes may be made to occur photochemically with ease. It is to be hoped that many of the techniques which have been developed for the study of reactions in solutions may be applied to the study of color center reactions, and that information so obtained will lead to a better understanding of the structure of these centers.

The high dilution of the solute implies that certain of the laws governing reactions in dilute liquid solutions may be expected to apply to these reactions; however, since the solvent enters the reaction in a very real way during the formation or destruction of color centers, we can hardly hope to draw many direct comparisons between reactions of this kind and those in liquid solutions without a precise knowledge of the role played by the host lattice in each particular process.

It is inviting to propose models and mechanisms to account for the interplay between the many absorption bands in the colored alkali halides, and also very stimulating to research because of the number of experiments performed to test such propositions. Students of these problems owe a great deal to SEITZ and others who have established a set of models for the M-, R-, Z- and V-centers, and their many associated centers, some of which were described in the preceding paper. These models, whether correct or not, are certainly the best that may be imagined on the basis of available evidence, and

it is significant that a large part of the phenomenal growth of interest in both the experimental and the theoretical aspects of the subject has occurred since SEITZ's review of the subject was published in 1946 ([1]). We must admit, however, that our knowledge of the reactions among color centers is really very rudimentary. In only a few isolated examples do we have even semi-quantitative data of the kind that the chemist would require in quantitative form before he would attempt to draw any conclusions about the mechanism or even the overall course of a reaction.

This is not a criticism of what has been accomplished or the methods of attack which have been used; the situation is a consequence of the experimental and theoretical difficulties which have been encountered, and of the limited number of laboratories engaged, mainly during the last few years, compared to the large number of investigators who have applied themselves to chemical processes in a systematic way for more than a century.

Two of the difficulties which must be overcome before reactions involving color centers may be put on a sound basis are the following: *a*) there is at present no analytical method which gives us with certainty the concentration of any one of the reacting species, and *b*) it is difficult to define, in a thermodynamic sense, what species are involved in a given process.

1. – Analytical Methods.

One of the first requirements in making a systematic study of a process is that we be able to determine accurately the concentrations of the reacting species before, during and after the process. In following the course of a color center reaction, it is customary to utilize the optical absorption characteristic of each center; if Beer's Law holds, we expect the concentration to be proportional to the absorption coefficient at any chosen wave-length. In the case of centers which absorb by electronic transitions, we have a theoretical relation which gives the constant of proportionality. The SMAKULA equation ([2]) gives nf in terms of the height and half-width of the absorption band. n is the concentration of centers and f is the oscillator strength for the optical transition. This relation, even though derived on the classical oscillator, is quite likely valid for certain color centers, as other absorption relations derived on the classical model turn out to be the same as those derived on the quantum mechanics.

However, we have still to determine f before the equation may be used to determine actual concentrations. For F-centers, it is likely that f is close to unity; for other centers the value can hardly be guessed at.

([1]) F. SEITZ: *Rev. Mod. Phys.*, **18**, 384 (1946).
([2]) A. SMAKULA: *Zeits. f. Phys.*, **59**, 603 (1930).

If sufficient alkali metal be added to an alkali halide so that its concentration may be measured by conventional chemical methods, then the absorption coefficient of F-centers is too high to measure in even the thinnest crystals which can be prepared for measurement, so that direct comparison of chemical and optical data is difficult to make. KLEINSCHROD ([3]) reported such a comparison, for which a value of 0.81 may be obtained for the oscillator strength of F-centers in KCl by the application of Smakula's equation. However, serious objections to Kleinschrod's method of chemical analysis may be raised, which make it appear fortuitous that f was found to have a value near the expected value of unity.

KLEINSCHROD measured the change in transmission of methyl red indicator in a slightly acid solution upon dissolving additively colored KCl, and compared the change with that produced by adding small amounts of KOH solution. From the large change in transmission produced by very small amounts of KOH, we may infer that the initial pH of the solution was in the neighbourhood of the pH for methyl red, which is 5.1. At this pH, the action of CO_2 absorbed from the air would not cause a serious error. However, there is a large effect on the color of the indicator to be expected from adding the KCl in addition to that due to the excess alkali metal in the form of color centers. While a neutral salt has a very small effect upon the absorption characteristics of the colored forms of methyl red ([4]), the concentration of the indicator species and of hydrogen ions will be markedly altered through the change in activity coefficients brought about by the large change in salt concentration.

The equation for the dissociation of the indicator may be written

$$\mathrm{MeH} = \mathrm{Me}^- + \mathrm{H}^+ ,$$

where MeH represents the red form, which is actually a zwitterion, and Me^- represents the yellow form. Then

$$K = C_{\mathrm{H}^+} \cdot \gamma_{\mathrm{H}^+} \frac{C_{\mathrm{Me}^-} \cdot \gamma_{\mathrm{Me}^-}}{C_{\mathrm{MeH}} \cdot \gamma_{\mathrm{MeH}}} ,$$

in which C represents the concentration and γ the activity coefficient. The data of KOLTHOFF ([5]) may be interpreted by assuming that γ_{Me^-} and γ_{MeH} remain about equal during changes in the ionic strength of a solution of methyl red. Reduction of γ_{H^+} by the addition of KCl will, if the indicator concentra-

([3]) F. G. KLEINSCHROD: *Ann. der Phys.*, 27, 97 (1936).
([4]) A. THIEL and G. COCH: *Z. anorg. allgem. Chem.*, 217, 353 (1934).
([5]) I. M. KOLTHOFF: *J. Phys. Chem.*, 32, 1820 (1928).

tion is small compared to C_{H^+}, result in an increase in the ratio $C_{\mathrm{Me}^-}\ C_{\mathrm{MeH}}$, that is, in the ratio of the yellow to the red color of the indicator. If C_{H^+} is small compared to the indicator concentration, the addition of KCl will have much less effect upon the color ratio, but will increase C_{H^+} markedly. If the original acid concentration is comparable to the indicator concentration, the increase in C_{H^+} would serve to offset the increase in the basic color.

In Kleinschrod's experiments, where the mean ionic activity coefficient for the dissolved KCl was as low as 0.80, calculations show that these effects may well be more important than the effect of the excess alkali metal in the colored crystals; however, it is possible that through the fortunate choice of original pH and indicator concentration the errors arising from the salt effect about cancelled each other.

It thus appears that further experiments to determine f for F-centers should be performed. Kleinschrod's method, modified to take into account the salt effect and making use of modern instruments, may prove valuable, but in addition techniques not based upon acidity changes in solution should be investigated.

2. – Definition of Species.

For many reactions occurring in liquid solutions, we may write stoichiometric equations involving only those species which have been shown to actually enter the reaction. The decision as to which species should be included, and what formulas should be used to represent them, is usually based upon a study of the effect upon the point of equilibrium of changes in the concentration of substances present in the reacting system. The variety of absorbing centers, vacancies, aggregates of vacancies, impurity atoms, and complexes in a colored alkali halide crystal make it difficult to apply such methods to equilibrium reactions involving color centers, since the concentration of any particular species may be governed by several equilibrium relations which must be satisfied simultaneously. Further there are only a few species, such as F-centers and added impurity atoms, whose concentration can be altered arbitrarily. Finally, such methods are of course not applicable to the many reactions of interest which occur irreversibly.

In spite of the difficulties outlined, some progress has been made toward an understanding of certain reactions of color centers. To illustrate the foregoing remarks and to show how such investigations have provided some insight into the nature of these centers, a few examples will be mentioned. We will concern ourselves only with additively colored crystals, for which the number of excess electrons is conserved during processes of conversion.

3. – Conversion of F- to M-Centers.

When a crystal containing F-centers is illuminated with light of a wave length lying within the F-band, part of the F-centers are converted into M-centers, which absorb at a greater wavelength. PETROFF (6) has made a study of the photochemical reaction. No information leading to a stoichiometric equation for the process is provided by his observations, but an interesting result bearing upon the mechanism of the conversion was obtained. The rate of growth of the M-band for a unit rate of absorption of energy increased after an initial period of illumination, and then remained constant. After destroying all of the M-centers by heating and irradiating with red light, the rate of M-band growth upon further illumination with light in the F-band retained the constant value that it had at the end of the first irradiation. It is clear that some sort of intermediate center is produced during the initial irradiation of F-centers which is stable toward the heating and red light illuimination. Experiments now being performed at the University of Illinois on the bleaching of F-centers under varying conditions, such as after cold-working to increase the concentration of defects, will undoubtedly add further to our knowledge of the mechanism of this conversion.

M-centers are also produced, in the absence of irradiation, during the additive coloring of crystals, and a thermal equilibrium has been found to exist between F- and M-centers (7). Assuming the validity of Beer's Law for both types of center, it was shown that, over a wide range of concentrations, the ratio of M-center to F-center concentration was a constant at constant temperature. The absolute value of the constant is unknown because of our uncertainty of the proportionality constant connecting absorption coefficient with concentration; however, it is clear that one M-center is produced for every F-center which is destroyed. This is the expected result if the model of the M-center proposed by SEITZ (1) is the correct one. Whether other species such as vacancies or impurities enter the reaction also cannot be determined from the results of this experiment.

If the relative values of the equilibrium constant for the reaction were known at one or more temperatures, an absolute value for the enthalpy change could be found. Thus we see that although lack of precise knowledge of the value of f for the centers involved precludes the determination of the actual value of the equilibrium constant, we are able to obtain both the coefficients for the reacting species and the heat of the reaction.

(6) S. PETROFF: *Zeits. f. Phys.*, **127**, 443 (1950).
(7) W. A. SMITH and A. B. SCOTT: *J. Chem. Phys.*, **21**, 2096 (1953).

4. – Formation of F'-Centers.

The photochemical conversion of F-centers to F'-centers was one of the first color reactions to be studied in a qualitative way. Pick ([8]), using the value of f given by Kleinschrod's analysis, found the quantum yield for the decrease in number of F-centers to be 2 F-centers per photon at -100 °C in KCl. Experiments on the photoconductivity of colored KCl have also been interpreted to show that when F-centers are ionized by light, the photoelectrons produced can be trapped on other F-centers to form F'-centers; at -100 °C such centers are fairly stable. This process would account for the quantum yield of 2, and gives some additional support to the validity of f used in the determination. Pick also found that the maximum quantum yield in colored NaCl for the reaction, assuming $f=1$, was 1.4; this datum may indicate that f for F-centers in NaCl is actually 0.7, if the reaction proceeds according to the same mechanisms as in KCl.

5. – Conversion of F- to Z_1-, and Z_2-Centers.

Chiarotti, Fumi and Giulotto ([9]) have performed and describe partly elsewhere in these proceedings, a set of experiments or processes occurring in alkali halides containing not only F-centers but added divalent ions. Considerable progress toward understanding the nature of the Z-centers has been made as a result of the study of these reactions.

6. – Coagulation of F-Centers to Colloid.

When an alkali halide is heated in the vapour of an alkali metal and then rapidly cooled to room temperature, the concentration of F-centers may be considerably higher than that which the crystal would retain at equilibrium at the lower temperature. Heating at some intermediate temperature, for example, 300 °C, will accelerate the coagulation of the excess F-centers into colloidal metal particles and a state of equilibrium between the F-centers and the colloid may be established at the intermediate temperature ([10]).

The equilibrium concentrations of F-centers as a function of temperature

([8]) H. Pick: *Ann. der Phys.*, **31**, 365 (1938).

([9]) P. Camagni, G. Chiarotti, F. G. Fumi and L. Giulotto: *Phil. Mag.*, **45**, 225 (1954); G. Chiarotti, F. G. Fumi and L. Giulotto: *Proceedings of the Bristol Conference on Lattice Defects in Solids* (Bristol, July 13-17, 1954).

([10]) A. B. Scott, W. A. Smith and M. Thompson: *J. Chem. Phys.*, **57**, 757 (1593).

were obtained for KCl, KBr, KI, and NaCl, using a value of $f=1$, and from these the heat absorbed in the dissociation of metal into F-centers was calculated. The rate of coagulation has also been investigated as a function of temperature ([11]), and an approximate activation energy for the migration of F-centers was provided.

7. – Conclusion.

Although it is not likely that reactions involving color centers will ever be put on the precise thermodynamic basis of many reactions in liquid solutions where in many cases it has been possible to determine not only all of the species taking part in the process but their chemical activities as well, quantitative studies of the kind outlined here have proved useful in solving the problem of the composition of several absorbing centers. There remain many reactions, such as those involving the R- and N-centers and the several varieties of V-centers, particularly in crystals containing an excess of halogen, for which systematic investigations have yet to be made.

* * *

The generous assistance of the Guggenheim Memorial Foundation during the period in which this paper was prepared is gratefully acknowledged.

([11]) F. THEISEN and A. B. SCOTT: *J. Chem. Phys.*, 20, 529 (1952).

INTERVENTI E DISCUSSIONI

— F. SEITZ:

I wonder if there is any evidence in the experimental data which contradicts the hypothesis that the M centre is an excited state of the F centre in the sense that the entire lattice has higher energy.

— A. B. SCOTT:

I have no evidence to the contrary; however, I have no data on the temperature dependence of the equilibrium constant of the F centre to M centre reaction.

— F. SEITZ:

If the M centres should be associated with impurities in the lattice, a very high concentration would be required to ensure that the ratio of the intensity of the M band to that of the F band is constant even when the colouration is strong.

— A. B. Scott:

I agree.

— F. G. Fumi:

Have you given any thought to the observations of Hacskaylo, Groetzinger and their coworkers on the pH of alkali halides treated in various ways?

— A. B. Scott:

Unfortunately these authors did not measure the optical absorption of their crystals and thus their data do not allow one to estimate the oscillator strength.

— A. R. Ubbelohde:

I wonder if the work of Professor Scott throws any light on the phenomenon of colloid formation during the electrolysis of alkali halide melts.

— A. B. Scott:

The study of the alkali halide melts presents considerable technical difficulties among which there is the highly corrosive action of the alkali metals on the reaction vessels. My group at Oregon State, as well as other groups, has attempted to find colour centre absorption in alkali halide melts with no success. Of course, we would not expect to find the F centre in precisely the form in which we picture it in the solid.

Diffusion in Alloys.

R. Shuttleworth

University of Leeds - Leeds

[Testo non pervenuto. (*N.d.R.*)].

Experiments on the Z_2 Band (+).

G. CHIAROTTI, F. G. FUMI (*) and L. GIULOTTO

Istituto di Fisica dell'Università - Pavia

The Z bands are colour-centre absorptions connected with the presence of substitutional divalent cations in the alkali halide crystals. In the course of our work on Z bands, some results of which have already appeared in the literature (1), we have recently performed experiments on the Z_2 band in KCl crystals containing Sr^{++} impurities coloured additively. The main results we have obtained are as follows:

1) The Z_2 band is formed together with the F band if the crystal is cooled slowly enough from the temperature of colouration.

2) The Z_2 band can be obtained directly from the F band by heating the crystal at 110 °C in the dark.

3) The yield of the transformation $F \rightarrow Z_1 \rightarrow Z_2$ at 110 °C under the action of F light depends strongly on the velocity with which the crystal has been cooled from the temperature of colouration. The yield is greater in crystals cooled more slowly.

4) Experiments with light polarized along the cube axes of the crystal performed to confirm the planarity of the Z_2 centre, have revealed no dichroism.

The results 1) and 2) can be easily interpreted with the model proposed by SEITZ. The result 3) seems to require the hypothesis that the Z_1 centre ionizes thermally at 110 °C. Finally the result 4) appears to indicate that

(+) The complete text of this communication has appeared in the *Proceedings of the Bristol Conference on Lattice Defects in Solids* (Bristol, 13-17 July, 1954).

(*) Gruppo di Fisica dei Solidi, Istituto di Scienze Fisiche, Università di Milano.

(1) P. CAMAGNI, G. CHIAROTTI, F. G. FUMI and L. GIULOTTO: *Phil. Mag.*, **45**, 225 (1954); P. CAMAGNI and G. CHIAROTTI: *Nuovo Cimento*, **11**, 1 (1954).

the orientation of the Z_2 centre may be different from that proposed by SEITZ. The lattice positions of the divalent impurity and of the positive- and negative-ion vacancies which are thought to compose the centre could be respectively (000), $\left(\frac{a}{2}\frac{a}{2}0\right)$ and $\left(\frac{a}{2}\frac{a}{2}\frac{a}{2}\right)$ (a, lattice parameter).

The research reported in this communication was supported by grants from the Consiglio Nazionale delle Ricerche.

INTERVENTI E DISCUSSIONI

— F. SEITZ:

I agree that your model for the Z_2 centre is quite plausible since it is reasonable that the negative-ion vacancy may try to stay farther from the divalent ion while still sharing the electron with it. In any case I imagine you intend to pursue the experiments with polarized light to check this model.

— A. B. SCOTT:

I wonder if you have observed any effect of the cooling rate on the Z_1 band.

— G. CHIAROTTI:

A study of this effect has not yet been made but we intend to do it in the near future.

— G. CINI:

Do you think that paramagnetic absorption can yield useful informations on the structure of Z centres?

— G. CHIAROTTI:

A measure of the g value for the Z_1 centre would have some interest. The g value for the Z_1 centre accepting Seitz's model should differ slightly from the g value for the F centre.

Calculations on the Interactions between Equilibrium Defects in the Alkali Halides (+).

F. BASSANI (*) and F. G. FUMI (*)

Istituto di Scienze Fisiche dell'Università - Milano

Let us consider an alkali halide crystal containing positive and negative-ion vacancies and positive divalent impurities which enter the alkali lattice substitutionally. These lattice defects interact roughly in a Coulomb-like fashion and it is reasonable to expect that owing to this interaction some of these defects are associated into neutral complexes. The most important neutral

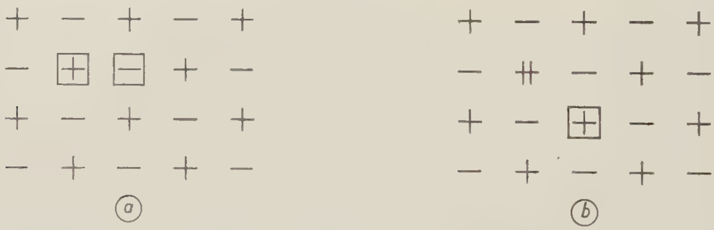


Fig. 1.

complexes are considered to be: *a*) a positive-ion vacancy in the position of nearest neighbour of a negative-ion vacancy; and *b*) a positive-ion vacancy in the position of next-nearest neighbour of a divalent impurity ion (Fig. 1).

The available experimental evidence for the existence of neutral complexes, particularly the vacancy pairs, is as yet somewhat indirect [1]. Thus it is difficult to obtain from existing data alone quantitative informations as to how, and in which quantity, defects are associated into complexes, and even more

(+) A detailed account of the work described in this communication will appear in a paper to be published in the near future.

(*) Gruppo di Fisica dei Solidi, Sezione di Milano dell'I.N.F.N..

(1) See, for instance, F. SEITZ: *Rev. Mod. Phys.*, **26**, 7 (1954).

so to obtain quantitative information on the interactions between defects at greater distances. It is therefore of interest to perform theoretical calculations on these interactions. Our work is aimed at finding how far the lattice theory of ionic crystals ([2,3]) allows one to progress significantly along this line.

The principal uncertainty in these lattice calculations lies perhaps in the numerical values for the parameters which enter the repulsive energy between ions. This energy is well represented by a function of the type $c_{12} b \exp[(r_1 + r_2 - r)/\varrho]$, where c_{12} is a constant which depends on the charges of the interacting ions, r_1 and r_2 are lengths typical of the ions, and b and ϱ are parameters which should be universal. Alternative approaches are possible in dealing with these parameters. BORN and MAYER take for r_1 and r_2 the values given by GOLDSCHMIDT and determine b and ϱ from empirical data; HUGGINS and MAYER ([4]), instead, assume $b = 10^{-12}$ ergs, adopt the average ϱ calculated by BORN and MAYER for the alkali halides and determine empirically by an iteration procedure r_1 and r_2 dealing at once with all the alkali halides. Finally MOTT and LITTLETON consider only repulsive interactions between nearest neighbours and eliminate $b \exp[(r_1 + r_2)/\varrho]$ by using the equilibrium equation between electrostatic and repulsive forces in the perfect crystal: they are thus left only with the parameter ϱ for which they adopt essentially the values of BORN and MAYER. Another unsatisfactory feature of the calculations performed so far on lattice defects in ionic crystals is the usage of polarizabilities for free ions ([5]): however, values for the polarizabilities of ions in alkali halide lattices are now available ([6]) and will be used in future work.

The lattice energies of the alkali halides and the energies to remove positive ions are relatively insensitive to the form one chooses for the repulsive potential. Table I compares the values (in eV) we have computed for the

TABLE I.

	M.L.	B.M.	H.M.
NaCl	4.62	4.65	4.53
KCl	4.47	4.35	4.31

work to remove a positive-ion to infinity from NaCl and KCl crystals using the BORN-MAYER (B.M.) and HUGGINS-MAYER (H.M.) potentials with the

([2]) M. BORN and M. GOEPPERT-MAYER: *Hand. d. Phys.*, **24** (2), 623 (1933).
([3]) N. F. MOTT and M. J. LITTLETON: *Trans. Faraday Soc.*, **34**, 485 (1938).
([4]) M. L. HUGGINS and J. E. MAYER: *J. Chem. Phys.*, **1**, 643 (1933).
([5]) L. PAULING: *Zeits. f. Krist.*, **67**, 377 (1928).
([6]) W. SHOCKLEY, J. R. TESSMAN and A. H. KAHN: *Phys. Rev.*, **92**, 890 (1953).

values (in eV) reported by MOTT and LITTLETON (M.L.). The work to remove a negative ion, instead, is affected as much as $\frac{1}{2}$ eV by the type of repulsive potential that is used. Thus the latter is not a quantity which can be calculated very reliably by ionic lattice theory.

The binding energies of a vacancy pair and of a divalent impurity-positive ion vacancy complex can be computed by calculating only energies to remove positive ions. Indeed the binding energy of the impurity complex is simply the difference of the work to create a positive-ion vacancy in the perfect lattice and the work to create it in the position of next-nearest neighbour of a divalent ion (7). Similarly the association energy of a vacancy pair is given by the difference of the work to create a positive-ion vacancy in the perfect lattice and the work to create it in the position of nearest neighbour of a negative-ion vacancy. The values we have obtained for the binding energy of a vacancy pair are 0.66 eV in NaCl and 0.85 eV in KCl: the value 0.89 eV reported by REITZ and GAMMEL (8) for NaCl must be considered inaccurate owing to internal inconsistencies of the calculation. The association energy of a vacancy pair is somewhat larger in KCl as one should expect since the outward distortion around a negative-ion vacancy is smaller in KCl than in NaCl.

+	−	+	−	+	−
−	$\boxed{+}$	−	⧺	−	+
+	−	+	−	+	−
−	+	−	+	−	+

Fig. 2.

It is physically obvious and can be shown analitically that at large distances the interaction between a pair of vacancies and between an impurity and a vacancy is Coulombic. Since the binding energy in the « ground state » of the vacancy pair and of the impurity complex is smaller than the Coulombic value, it is of interest to see how quickly the interaction energy approaches the Coulombic value. To achieve this end, calculations have been undertaken by Mr. TOSI on the binding energy of the « first excited state » of the impurity complex, namely on the interaction between a divalent impurity in a (000) lattice position and a vacancy in the (200) lattice position (Fig. 2). The preliminary results give the surprising answer that the interaction energy is larger than the Coulombic value by a factor between 1 and 2; it seems likely that the result is to be imputed to the usage of the large polarizability for the free Cl^- ion as one can envisage from Fig. 2. Accordingly the calculations will be repeated with the polarizabilities appropriate to ions in an alkali halide lattice (*). In any case these preliminary results seem to indicate that the inter-

(7) F. BASSANI and F. G. FUMI: *Nuovo Cimento*, **11**, 274 (1954).

(8) J. R. REITZ and J. L. GAMMEL: *J. Chem. Phys.*, **19**, 894 (1951).

(*) *Note added in proof*: Tese calculations have now been performed and have confirmed our expectations. The binding energy of the « first excited state » of the

action energy between lattice defects approaches very quickly the Coulombic value, so that it appears legitimate to take this energy as Coulombic at all distances except the distance of closest approach (9).

The research reported in this communication was supported by a grant from the Consiglio Nazionale delle Ricerche.

impurity complex is still somewhat smaller then the Coulombic value, especially in KCl: the « ground-state » binding energy is practically not affected by the change in polarizabilities.

(9) A. B. LIDIARD: *Phys. Rev.*, **94**, 29 (1954).

INTERVENTI E DISCUSSIONI

— F. SEITZ:

Have you found in your recent calculations any justification for the apparent lack of association in Calcium doped NaCl, reported by BEAN?

— F. BASSANI:

The calculations on the association energy of divalent impurities and positive ion vacancies at next-nearest neighbour position would make one expect essentially equal behaviour for Ca^{++} and Cd^{++} impurities in NaCl. However, one should be rather careful in deriving conclusions from a simple association theory.

— F. G. FUMI:

It should be noted that the experimental evidence does not consistently point to a lack of association for Ca^{++} in NaCl. HAVEN, for instance, by measurements of dielectric loss definitely finds association for Ca^{++} in NaCl.

Preliminary Experiments on the Kirkendall Effect in Alkali Halide Crystals (*).

G. CHIAROTTI and F. G. FUMI (+)

Istituto di Fisica dell'Università - Pavia

We report here the preliminary results of experiments undertaken two years ago to observe the Kirkendall marker shift in the interdiffusion of single crystals of KCl and (K, Rb)Cl.

A large number of experiments have been performed on the Kirkendall shift in policrystalline couples of f.c.c. metals since Kirkendall and Smigelskas first observed it in the interdiffusion of copper and α-brass ([1]). The qualitative interpretation of the phenomenon based on the difference of the diffusion coefficients for the two species of metal atoms ([2]) and on the ability of dislocations to keep the concentration of thermal defects (vacancies and interstitials) at its equilibrium value ([3]) has basically withstood the test of these experiments. However, porosity has frequently been observed on the side of the sample which suffers a nett loss of atoms pointing to an inability of dislocations and grain boundaries to absorb fully the excess of vacancies present in the region ([4]).

We felt that the study of the Kirkendall shift in single crystals of alkali halides, where it is well known that the transport of matter occurs by a vacancy mechanism, could not only add to the limited knowledge of the

(*) This work is supported by grants from the Consiglio Nazionale delle Ricerche.

(+) Gruppo di Fisica dei Solidi, Istituto di Scienze Fisiche, Università di Milano.

([1]) For a review of this work, see A. D. LE CLAIRE: *Progress in Metal Physics*, **4**, 265 (London, 1953). Kirkendall shifts have recently been reported also for a b.c.c. phase (β-brass): U. S. LANDERGREN and R. F. MEHL: *Journ. of Metals*, **5**, 153 (1953); R. W. BALLUFFI: unpublished work.

([2]) L. S. DARKEN: *Trans. Amer. Inst. Min. Met. Engrs.*, **175**, 184 (1948).

([3]) F. SEITZ *Acta Cryst.* **3**, 355 (1950). See also N. F. MOTT, IX^e Conseil de Physique Solvay (Bruxelles, 1951), p. 519.

([4]) Recent discussions of this porosity have been given by F. SEITZ: *Acta Met.*, **1**, 355 (1953) and R. W. BALLUFFI: *Acta Met.*, **2**, 194 (1954).

properties of dislocations in these crystals [5], but perhaps also help in the understanding of the Kirkendall effect itself. The elimination of grain boundaries [6] and the inability of dislocations in the NaCl-type of lattice to split into stacking faults [7] should represent useful simplifications. We have chosen the system KCl-RbCl since it is known to give mixed crystals stable at room temperature for all compositions.

Each specimen used in the experiment consists of a small cubic crystal of (K, Rb)Cl 0.3 to 0.5 cm on a side coated with a crystal layer of KCl 0.1 to 0.2 cm thick: two Pt wires 0.002 cm in diameter mark a pair of opposite surfaces of separation. The mixed crystals are prepared from a melt of minimum freezing temperature (30% KCl+ +70% RbCl) to ensure homogeneity of composition. A Pt wire is then wound around the mixed crystal and a layer of pure KCl is deposited on the mixed crystal from a saturated KCl solution by slowly lowering its temperature. The specimen obtained is cut on both sides following a cube face parallel to the axis of winding of the Pt wire.

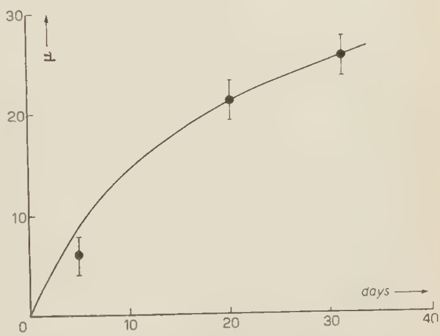


Fig. 1. – Decrease in wire distance vs. annealing time at a temperature of 630 C°.

To allow diffusion to occur, the specimens are then annealed at about 600 °C in air or in vacuum for a period between 5 and 30 days. The distance between the two Pt-wire markers is measured before and after diffusion with a micrometer comparator: the mean error is evaluated from 100 measurements and is about $\pm 2\ \mu$.

The measurements performed so far have *always* revealed upon diffusion a shift of the markers toward the mixed crystal, which is the phase of lower melting point. The observed shifts are thus in the direction predicted by the empirical rule for Kirkendall shifts [8].

Some typical results are given in Fig. 1 where the decrease in the distance between markers is plotted as a function of the time of annealing in air at

(5) The properties of dislocations in the alkali halides are discussed by F. SEITZ: *Phys. Rev.*, **80**, 239 (1950); *Rev. Mod. Phys.*, **26**, 7 (1954).

(6) It should be noted that Kirkendall shifts have already been observed in policrystalline metallic samples of large grain size (3-15 mm): W. SEITH and A. KOTTMANN: *Naturwiss.*, **39**, (2), 40 (1952).

(7) F. C. FRANK and J. F. NICHOLAS: *Phil. Mag.*, **44**, 1213 (1953), section 3.4.

(8) L. C. CORREA DA SILVA and R. F. MEHL: *Trans. Amer. Inst. Min. Met. Engrs.*, **191**, 155 (1951).

630 °C. Other measurements on crystals annealed in air or in vacuum have given similar results. The shifts are roughly proportional to $t^{\frac{1}{2}}$ (t, annealing time) but rather strong deviations from this proportionality (up to 50%) are observed at times: similar deviations have been reported also for the Kirkendall marker shifts in policrystalline metallic specimens [9]. While it is difficult to predict the values of the Kirkendall shifts to be expected for our couples, the observed shifts appear of a reasonable order of magnitude.

The results we have obtained so far are still meagre because there is a fair chance for the specimen to break during the annealing time. After annealing the surface of the specimen appears altered. At present it is not possible to state what influence these alterations could have on our measurements. Further experiments are in progress to make the results more reliable.

[9] U. S. LANDERGREN: *Rates of Diffusion and Marker Movements in Beta Brass* (Ph. D. Thesis, Carnegie Institute of Technology, 1953), p. 83-87.

INTERVENTI E DISCUSSIONI

— F. SEITZ:

It is likely that in your Kirkendall experiments, matter transport may occur by vacancy pairs to obviate the setting up of a field due to the difference in diffusion coefficients of K^+ and Rb^+. Thus it may be of interest to study also the ionic conductivity of your samples.

— F. G. FUMI:

I quite agree that this could be a case where matter transport by vacancy pairs may be dominant. A check of the validity of the Einstein relation could thus have considerable interest.

— A. R. UBBELOHDE:

In a series of theoretical and experimental papers WASASTJERNA and coworkers claimed that solid solutions of mixed alkali halides show partial segregation of the dissimilar ions, particularly below a critical temperature. If such partial segregation occurs, diffusion in such partially ordered solids may show complicated effects, particularly if the segregation involves a change of volume. It is no longer quite straightforward to speak of the mobility of K^+ and Rb^+ ions within the mixed crystal. If there is partial segregation macroregions of the crystal have to be considered in order to describe ionic movement completely. Any observation on the Kirkendall effect in mixed crystals is of great interest in such systems, though interpretation may be more complicated than for homogeneous solid solutions.

— F. SEITZ:

GNAEDINGER searched for order in the mixed crystals of the alkali halides which he investigated in his well known study of F centers. He has informed me that no effects which might be ascribed to order could be found.

— F. G. FUMI:

It seems to me that SEITZ's remark answers very well UBBELODHE's point. Indeed a study of colour centre absorption in the mixed crystals of the alkali halides such as that of GNAEDINGER, or that of MEISSNER and PICK, provides a rather sensitive method to test for the absence of local order. It should perhaps also be recalled that even according to WASASTJERNA and coworkers the system KCl + RbCl that we chose for study, and which is one of those studied by GNAEDINGER and by PICK, has its critical temperature well below room temperature (~ -70 °C).

SUPPLEMENTO AL VOLUME I, SERIE X DEL NUOVO CIMENTO N. 2, 1955

Sull'energia di attivazione del fenomeno di diffusione dell'azoto nel Fe-α.

I. BARDUCCI

Istituto Nazionale di Ultracustica - Roma

Come è noto la dipendenza della costante di diffusione dalla temperatura può essere studiata con precisione relativamente grande, e su un campo di temperatura assai esteso, nel caso delle soluzioni solide interstiziali nei reticoli cubici a corpo centrato.

Per tali soluzioni solide, infatti, i normali metodi adoperati per la misura della costante di diffusione in volume e validi per le temperature elevate, possono essere integrati, nel campo delle temperature più basse, da altri metodi di misura, che utilizzano in vario modo i fenomeni di rilassamento elastico legati alla diffusione su scala atomica.

Sono stati finora studiati, nel modo ora esposto, diversi sistemi binari, ed in modo particolare le soluzioni solide di C ed N nel Fe-α. Il campo di temperature esplorato, nei due sistemi suddetti ha, tuttavia, un'estensione notevolmente diversa.

Mentre infatti, le soluzioni solide di C in Fe-α sono state studiate nell'intervallo di temperature compreso fra circa -35 e $+700$ °C, nel caso dell'N in Fe-α lo stesso intervallo varia soltanto fra circa -30 e $+35$ °C.

La corrispondente precisione nella misura della energia di attivazione H e della costante D_0 risulta pertanto assai minore.

WERT ha inoltre mostrato che i dati sperimentali, se confrontati con quelli calcolati in base a considerazioni teoriche, sembrano accordarsi assai meno bene per il sistema N in Fe-α che per quello C in Fe-α. Una estensione nel campo di temperature esplorato per il primo sistema si presentava pertanto come assai interessante.

Misure sul sistema N – Fe-α sono state compiute dall'autore in collaborazione col dott. ing. P. GENCE, mediante tre diversi apparati che consentono la misura dell'attrito interno in funzione della temperatura e della frequenza;

due dei quali esistenti presso l'Istituto di Ultracustica in Roma, il terzo presso il Conservatoire National des Arts et Métiers di Parigi.

Tali misure, unite ai dati già esistenti, hanno permesso di portare il limite superiore dell'intervallo di temperatura fino a circa 200 °C.

Il suddetto intervallo è perciò meno esteso che nel caso della soluzione solida di C in Fe-α: tuttavia la corrispondente variazione della costante di diffusione risulta di otto unità logaritmiche, anzichè di tre come nelle misure di WERT.

Sebbene sia presumibile che la precisione ottenuta nelle misure risulti così notevolmente aumentata, i valori ottenuti da WERT, e cioè $H = 18\,200$ cal/mole e $D_0 = 3 \cdot 10^{-3}$ cm^2/s, restano però perfettamente confermati dalle nostre misure, cosicchè l'accordo con la teoria appare tuttora meno soddisfacente che nel caso della soluzione solida di C in Fe-α e di qualche altro sistema binario.

Un accurato esame della questione ha consentito, tuttavia, di concludere che, eseguendo il confronto fra dati teorici e sperimentali sulla base di parametri più direttamente misurabili di quello scelto da WERT (entropia di attivazione), il già rilevato disaccordo con la teoria appare contenuto nei limiti che ci si possono attendere ammettendo una ragionevole precisione di misura: una verifica più precisa dei risultati teorici appare perciò tutt'altro che agevole.

INTERVENTI E DISCUSSIONI

— P. G. BORDONI:

I would like to hear some discussion on other applications of the anelastic technique used by BARDUCCI to studies of diffusion in metals, perhaps also of f.c.c. structure.

— R. SHUTTLEWORTH:

It would be useful to study the diffusion of S in Fe since it is not yet known whether it is interstitial or not.

— F. G. FUMI:

I should like to call attention to the work of NOWICK who has observed internal friction peaks related to diffusional ordering for substitutional solutions of f.c.c. structure: specifically the Ag-Zn α phase. Earlier work had been done by ZENER and KÊ on 70-30 α brass. Considerably higher concentrations of solute are needed to observe an effect in the substitutional solutions of f.c.c. structure than in the interstitial solutions in b.c.c. lattices because the elastic distortion around single substitutional impurities has still cubic symmetry.

An Electroacustical Study on Cold-Working and Recrystallization of Aluminium.

F. Gatto

Istituto Sperimentale dei Metalli Leggeri - Novara

The measurement of elastic constants by electroacoustic or ultrasonic methods can be applied for studying the phenomena connected with cold-working and recrystallization of metals.

In this way we may hope to increase our knowledge on this subject, by getting new information in addition to the experimental evidence obtained by the classical methods of mechanical tests and X-ray techniques.

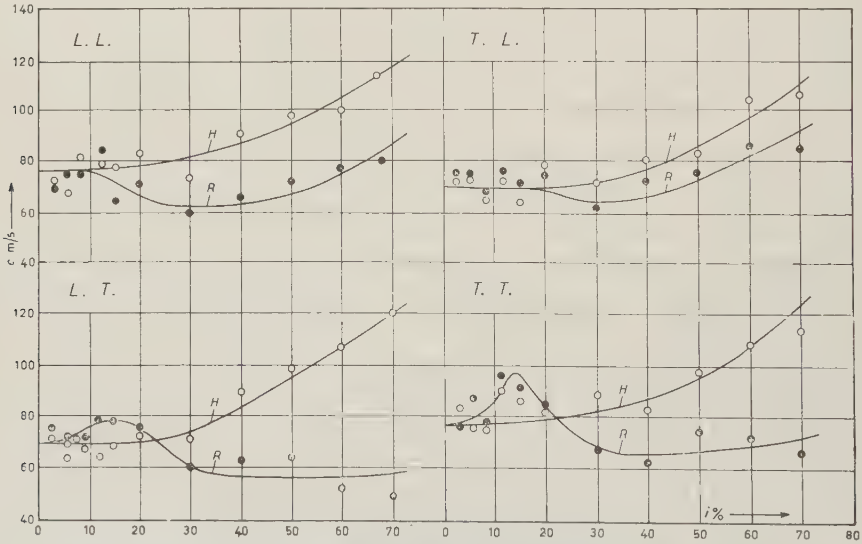


Fig. 1. - Sound velocity in Aluminium sheets, cold-rolled (H) and later annealed (R):

diagram	*rolling direction*	*specimen cut*
L.L.	longitudinal	longitudinally
L.T.	longitudinal	transversally
T.L.	transversal	longitudinally
T.T.	transversal	transversally

Starting research in this field, we obtain some experimental results testing cold-rolled sheets and wires drawn of aluminium (Al 99.5). We determine the sound velocity for longitudinal waves (25 kHz) in annealed materials; later, inducing different amount of cold-working by means of cold-rolling, wire-drawing, or by applying tensile deformation, we measure the change of sound velocity, induced by cold-working.

We obtain in each case an increase of sound velocity which appears to be very nearly a linear function of the amount of deformation induced by cold-working when the latter exceeds 40 % (Fig. 1). This effect is not one of increase in density of dislocations because the dislocations, and the elastic energy near dislocations, induce a decrease, never an increase, of the velocity of sound which is less than 0.1 %.

The effect is one of modification of orientation of the annealed materials.

We then anneal the specimens (360 °C/4 h) testing them again, and we find that the final value of the sound velocity is related to the type of plastic deformation to which the material has been previously subjected (Fig. 1). From the evidence obtained we conclude that the velocity variations are related to the crystalline orientation.

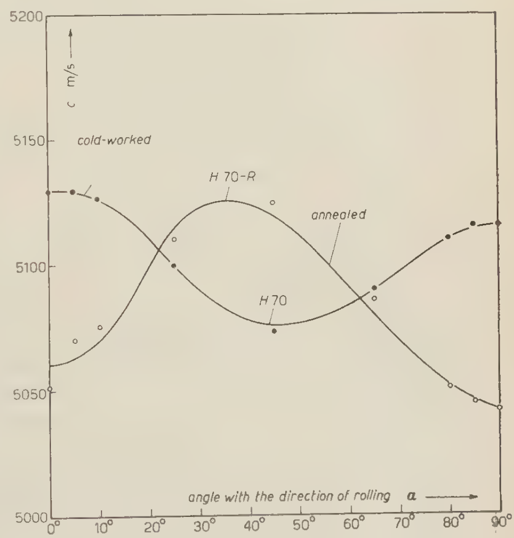


Fig. 2. – Anisotropy of the sound velocity.

Finally we measure the sound velocity on specimens cut with different orientations from a sheet. We are so able to determine the degree of anisotropy of the sheet before and after annealing (Fig. 2).

The evidence obtained appears to agree with the mechanism of cooperative rotation of atoms proposed by KRONBERG and WILSON to explain the change of crystal orientation induced during the secondary recrystallization.

INTERVENTI E DISCUSSIONI

— F. SEITZ:

Have you determined the orientation of your samples with X-rays?

— F. GATTO:

No, I have not.

Transport Phenomena in Melts and the Mechanism of Melting.

A. R. Ubbelohde

Imperial College of Science and Technology - London

1. – The Nearest Neighbour Description of Melts.

From time to time new aspects are developed of the theme that liquids are quasi-crystalline, especially near the freezing point and far from the critical temperature [1]. However, with « simple » spherically symmetric units, experimental information is mainly restricted to evidence that the number and distribution of nearest neighbours to any unit of structure does not greatly change on melting. On this basis it is possible, for example, to account for the spacing of the « liquid ring » in X-ray diffraction pictures of melts, and the fact that the specific heat of many melts lies close to that of the crystalline phases.

2. – Anisotropic Polymethylene Molecules.

Except in the case of ionic melts, discussed below, for liquids composed of units which are effectively spherically symmetrical, it seems difficult to go much further in studying the physical properties of melts. But when the units of structure are markedly anisotropic, there is considerable evidence that the quasi crystalline structure of the melt requires much more than a discussion of nearest neighbours for its description. It is convenient to refer to the « middle-range » structure of melts, when discussing the molecular packing in

(1) Cf. references in A. R. Ubbelohde: *Quart. Rev. Chem. Soc.*, **4**, 356 (1950).

regions between the « nearest neighbours », and « long range order » such as prevails in crystals. The significance of middle range structure has been realised for some time in the case of crystals and melts of polymethylene compounds. For example, X-ray diagrams of the melts of a series of homologous alcohols show diffraction rings corresponding with several repeat intervals, indicating that groups of molecules are stretched out and roughly parallel in the melt, in what Stewart termed « cybotactic » clusters (2) (Fig. 1). The change in volume of polymethylene compounds on melting (3) is far too small to permit a random distribution of all possible molecular configurations in the melt, such as might be found in the dilute vapour. This again indicates considerable adlineation into clusters. The specific heats of crystals and melts (1) and various premelting phenomena, likewise indicate that for this class of anisotropic molecules the structure of the melt is far from being isotropic, over small numbers of molecules, near the freezing point. However, polymethylene molecules present an extra complication in discussing mechanisms of melting, because of their flexibility and ability to assume a number of configurations of practically the same free energy by crumpling through rotation about single C—C bonds (4).

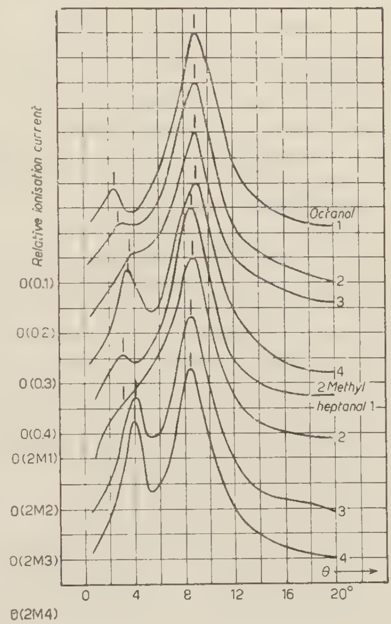


Fig. 1.

3. – Melting Mechanisms of Rigid Anisotropic Molecules.

In order to pursue the problem of middle-range structure in melts more closely, it is helpful to examine anisotropic units of structure which cannot take up a wide range of configurations by crumpling. Some form of chemical stiffening of the bonds is required, and when it is desired to compare molecules

(2) G. W. Stewart: *Chem. Rev.*, 6, 483 (1929); *Phys. Rev.*, 35, 726 (1930); G. W. Stewart and R. L. Edwards: *Phys. Rev.*, 38, 1575 (1931).

(3) H. Sackmann and P. Venker: *Zeits. Phys. Chem.*, 199, 100 (1952).

(4) J. C. McCoubrey and A. R. Ubbelohde: *Quart. Rev., Chem. Soc.*, 5, 364 (1951).

with only small differences of shape this stiffening is conveniently obtained by some form of bond conjugation in the molecule. Certain kinds of conjugation provide useful molecules from the geometrical standpoint, but with insufficient chemical stability to permit adequate thermal studies over a range of homologues and isomers. For example, there are the homologous polyenes $CH_3—(CH=CH)_n—CH_3$ which form stiff rod-like molecules. The melting points of such homologous series show unusual sequences (1) but up to the present the chemical properties have not encouraged thermodynamic work. Similar remarks apply to the acetylene homologues $CH_3—(C\equiv C)_n—CH_3$. To obtain adequate chemical stability, one direct way is to use certain conjugated aromatic systems. In the very specialised field of liquid crystals, various molecules of this kind have been found which give highly anisotropic melts, with regions of anisotropy large enough to polarise visible light in a distinctive way. However, practically all the molecules giving rise to liquid crystals are heavily loaded with polar groups. This complicates interpretation of structure. (One of the few hydrocarbons which has been reported to give a melt which is liquid-crystalline near the freezing point is p-pentaphenyl $C_6H_5—(C_6H_4)_4—C_6H_5$ (5)).

4. – Melting Mechanisms of Rigid Aromatic Hydrocarbons.

To avoid complications of interpretation which can arise when there are polar groups in the molecules, we have been studying various series of aromatic hydrocarbons of related structure, which are stiffened by conjugation. The two main groups to be discussed in the present paper are the « fused » aromatic ring hydrocarbons (with Dr. Al-Mahdi) and the polyphenyls (with Mr. Andrews).

5. – Thermodynamic Parameters of Melting.

Though the main purpose of this paper is to discuss transport phenomena, in particular the viscosity of the melts near the freezing point, it is useful to record some significant facts about the thermodynamic parameters of melting, for these very anisotropic molecules.

6. – Entropies of Melting.

These have not yet been determined in all the cases to be discussed.

Table I gives some of the results available on changes of heat content and entropy on melting.

(5) p-pentaphenyl. D. Vorländer: *Zeits. Phys. Chem.*, **126**, 471 (1927).

TABLE I.

Molecule	S_f (e.u.)	$(C_{\text{liq}} - C_s)/R$
Benzene	8.5	0.5
Naphthalene	13.1	2.2
Anthracene	14.1	—
p-Xylene	14.1	—
Diphenyl	13.0	—
Acenaphthene	13.6	
Phenanthrene	12.1	
Chrysene	14.9	—

7. – Volume Changes on Melting.

These are particularly important in giving information about the degree of randomisation of the molecular axes of these anisotropic molecules in the melts. Effectively complete randomisation may be referred to as « rotation » without specifying anything about kinetics. For practically all the molecules quoted below, the fractional increase of volume on melting is definitely too small to permit « rotation » of the molecules in the melt, even about the axis with smallest space demands. In some cases, such as o- and p-terphenyl, the increase in volume on melting is particularly small. (See Table II.)

From this information, a working model has been put forward to describe the behaviour of melts of rigid anisotropic molecules (6). Two important features are:

(i) In the melting mechanism, a contribution from entropy of vibration makes a significant addition to the total entropy of fusion. This hypothesis requires that in the crystal containing N atoms a substantial proportion of the $3N$ natural frequencies are too high to be fully active below the freezing point. In the melt the somewhat greater space available lessens intermolecular repulsions, and thus permits a substantial increase in vibrational free energy and vibrational entropy. One experimental test is that $(C_{\text{liq}} - C_s)/R$ must be appreciable on passing through the melting point. Unfortunately little is known about this quantity, but further experimental information is being obtained.

(ii) Clusters of roughly ordered molecules must be present in the melt, since there is no free rotation. However, since the volume coefficient of expansion α_{liq} is not abnormally larger for such ordered melts, than is found for

(6) A. A. K. AL-MAHDI and A. R. UBBELOHDE: *Proc. Roy. Soc.*, A **220**, 143 (1953).

Table II.

Molecule	% $\Delta V_f/V_s$ experimental	Minimum % $\Delta V_f/V_s$ for rotation about most favorable axis	$\alpha_{\mathrm{Hq}} \cdot 10^4/^{\circ}$
Benzene	13.4	6.5	—
p-Xylene	21.1	32.8	10.3
Naphthalene	16.7	7.9	7.5
2-3 Dimethyl-N	14.6	49.8	7.7
2-6 Dimethyl-N	18.2	30.7	8.5
Acenaphthene	14.6	5.5	7.9
Anthracene	16.8	60.7	8.3
Phenanthrene	8.7	52.8	5.6
Chrysene	12.4	56.0	7.4
Diphenyl	12.4	31.0	10.1
p-Terphenyl	18.7	140.0	9.2
m-Terphenyl	10.6	410.0	6.3
o-Terphenyl	9.45	208.0	7.3

spherically symmetrical molecules, the degree of cluster ordering does not appear to change very rapidly above the melting point.

Since the melts under discussion do not show liquid crystalline behaviour, regions of order must be smaller in extent than say 10^{-4} - 10^{-5} cm. No steep anomalies of volume change dV/dT have yet been found in any of the pure melts investigated, as might be expected if there were anything corresponding to a « rotational transition » in the liquid.

8. – Viscosities of the Melts of Rigid Anisotropic Molecules.

As is well known, the temperature dependence of the viscosities of many liquids with spherically symmetrical units can be represented by an equation of the form

(i) $$\log \eta = \log A + E/RT ,$$

where good straight line relationships are observed in many instances. The volume-viscosity dependence can be represented by a semi-empirical equation, due in the first instance to Batschinski (7) and interpreted by Herzog and Kudar (8):

(ii) $$1/\eta = C(V - \omega) ,$$

(7) A. J. Batschinski: *Zeits. Phys. Chem.*, **84**, 643 (1913).

(8) R. O. Herzog and H. C. Kudar: *a*) *Zeits. f. Phys.*, **80**, 217 (1933); *b*) *Trans. Faraday Soc.*, **29**, 1006 (1933).

where C is a constant, V is the specific volume, and ω is proportional to the repulsion volume of the molecules, so that $(V - \omega)$ represents the « free volume » in the liquid. As first shown by BATSCHINSKI, many liquids give straight line plots for relation (ii), over extensive ranges of the variables. HERZOG and KUDAR obtain the relationship

$$1/\eta = \frac{2.4\cdot 10^4}{V^{\frac{1}{3}}}\sqrt{\frac{M}{T}}\,(v-\omega) \qquad \text{(iii}a\text{)}$$

for spherically symmetric units.

However, if the molecules are very far from spherically symmetrical, neither of these simple relationships can be expected to hold, since the transport of momentum is likely to be a much more specialised process depending on the particular shape of the molecules. HERZOG and KUDAR have attempted to make some allowance for the change to be expected in equation (iii$a$). When the molecules are not rotating, they propose the equation (iii$b$) in which it may be noted the constant C is smaller:

$$1/\eta = \frac{1.3\cdot 10^4}{V^{\frac{1}{3}}}\sqrt{\frac{M}{T}}\,(v-\omega)\,. \qquad \text{(iii}b\text{)}$$

v is the specific volume and V the molar volume of the melt at the F.P.. A theory of the viscosity of melts in terms of the mechanical interaction of microcrystalline groups has been proposed by CHAIKIN [9], but the simplifications introduced make it not well suited to the melts of rigid anisotropic molecules. When extensive clusters of roughly ordered molecules are present in the melt, it seems unlikely that any of the theoretical models as yet proposed goes far enough to interpret the phenomena. This can be made clear by considering some of the experimental findings that are being obtained.

(i) For very large ordered clusters, such as are present in liquid crystals the effects of grouping in hindering rotation should be most marked. Nevertheless, the Batschinsky relationship appears to hold where tested, for p-ethoxybenzalamino α-ethyl methyl cinnamate and for p-anisal azophenol ethyl carbonate [8b]. This lends support to the view that even in melts where liquid cristallinity does not appear, smaller groups and clusters control the transport of momentum.

(9) S. CHAIKIN: *Physical. Zeit. Sowjetun.*, 9, 504 (1936).

The main difference between viscosities of melts in the region of liquid crystals, and in the region of clear melts, lies in a moderate relative displacement of the Batschinski curves above and below the clearing temperature. Around the clearing temperature there is a steep anomalous peak in viscosity of the melt ([10]) possibly due to turbulence. (Fig. 2).

(ii) For branched polyphenyls, the plot of $\log \eta$ against $1/T$ shows a steep departure from the straight line relationship with an abnormal increase in E_η as the melting point is approached. This can readily be seen from the contrast between p-, m- and o-terphenyl. (See Table III.)

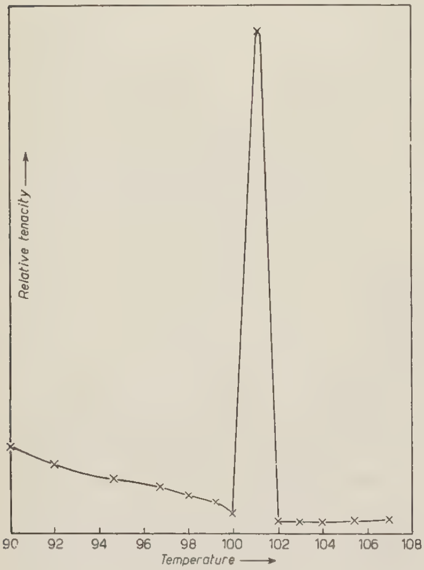


Fig. 2.

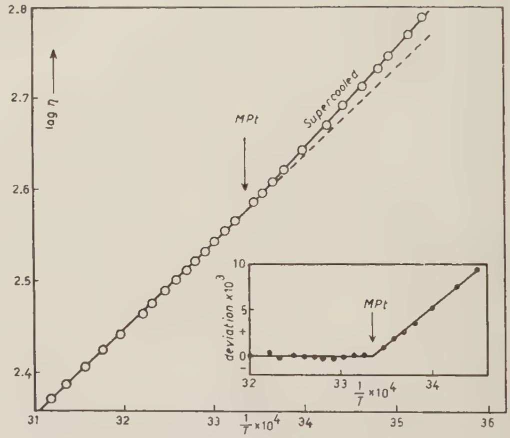
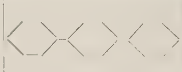
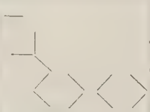
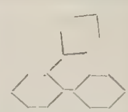


Fig. 3.

TABLE III. – *Momentum transport in phenyl and polyphenyl hydrocarbons.*

						
Around M.P.	E_η	2.63	3.80	3.76	7.40	16.04
	A_η	$7.19 \cdot 10^{-3}$	$5.43 \cdot 10^{-3}$	$1.64 \cdot 10^{-2}$	$1.73 \cdot 10^{-4}$	$7.41 \cdot 10^{-10}$
well above M.P.	E_η	2.42	3.41	3.76	5.34	7.93
	A_η	$1.01 \cdot 10^{-2}$	$9.59 \cdot 10^{-3}$	$1.64 \cdot 10^{-2}$	$2.70 \cdot 10^{-3}$	$9.95 \cdot 10^{-5}$

([10]) W. OSTWALD: *Trans. Faraday Soc.*, **29**, 1002 (1933).

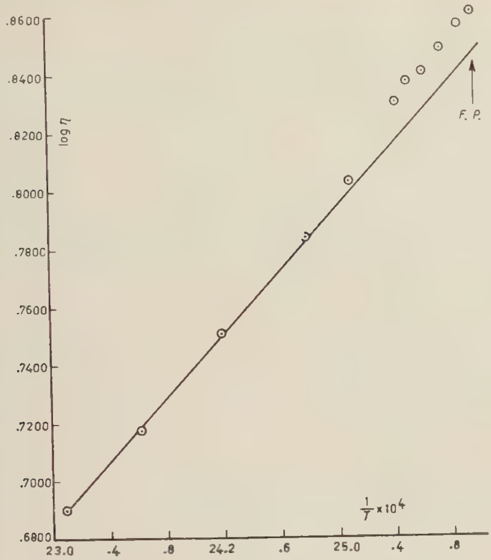


Fig. 4 *A*.

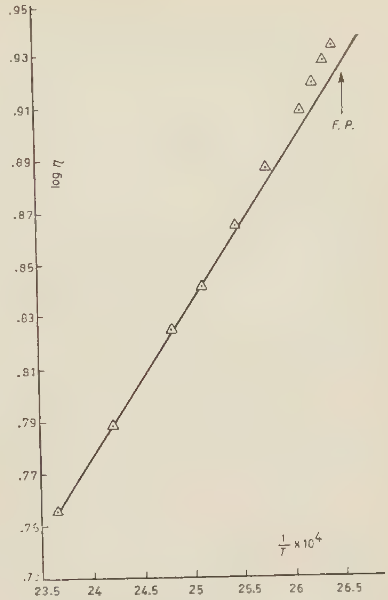


Fig. 4 *B*.

The quantities refer to the equation

$$\log \eta = \log A_\eta + E_\eta/RT\,, \qquad E_\eta \text{ is in kcal/mole.}$$

Other (polar) organic compounds show smaller departures from a linear relationship in the melt and there are likewise suggestive changes of slope somewhere near the melting point [11] (Fig. 3).

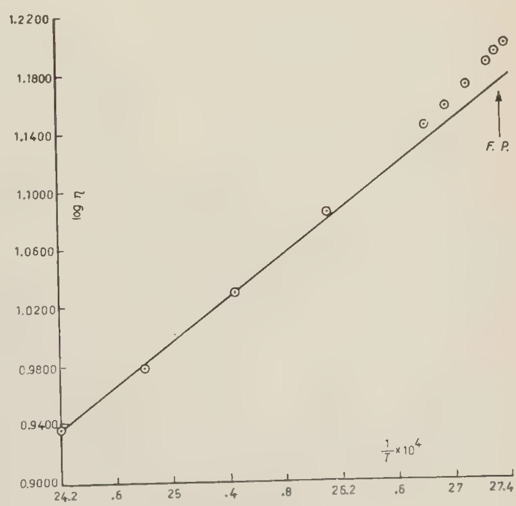


Fig. 5.

Melts such as o-terphenyl are nevertheless capable of very extensive supercooling. Since the viscosities are not exceptionally high, these possibilities for supercooling show that the interlocked clusters which increase in importance on cooling are incapable of acting as crystal nuclei. For crystallisation, a nucleating group requires a much more specific ordering of the molecules, than that which corresponds with the

(11) C. Dodd and Hu Pak Mi: *Proc. Phys. Soc.*, 62, 454 (1949).

interlocking groups present in large numbers in the melts as they are cooled.

For condensed aromatic hydrocarbons, the plots of $\log \eta$ vs. $1/T$ often show marked increases in E_η as the freezing point is approached, due to the increasing importance of the larger clusters. Fig. 4 A and B gives typical illustrations in the case of 2-3 and 2-6 dimethyl naphthalene, and Fig. 5 for acenaphthene.

(iii) If instead of using temperature as an independent variable, the fluidity $1/\eta$ of the melt is plotted as a function of specific volume, similar

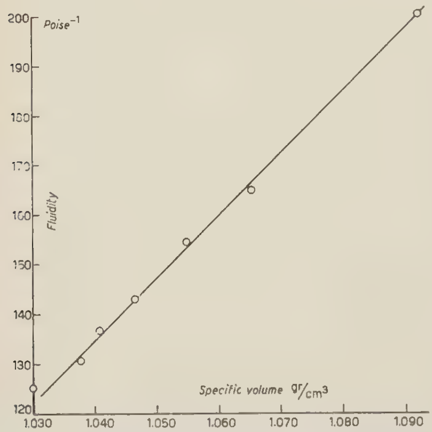


Fig. 6 A. – p-terphenyl.

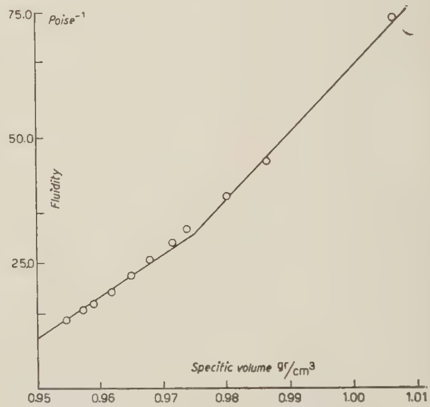


Fig. 6 B. – m-terphenyl.

indications are obtained of « interlocking » as the temperature of the melt approaches and traverses the freezing point. Departures from straight line plots are only slight for benzene, and are even smaller for p-terphenyl, where interlocking is presumably reduced by the closer adlineation of the molecules. But for the branched polyphenyls, there is extensive evidence of the change in the flow mechanism on approaching the freezing point (Fig 6, A,B,C).

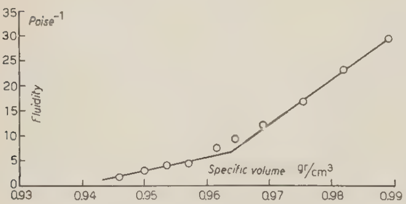


Fig. 6 C. – o-terphenyl.

For condensed aromatic hydrocarbons, deviations from the Batschinski straight line on approaching the freezing point are in the same sense as for the polyphenyls, but are less marked with the hydrocarbons listed. Details need not be given here.

(iv) An alternative way of investigating the momentum transport mechanism as a function of structure is to make use of the theory proposed for melts of spherical molecules, due to LAIDLER, GLASSTONE and EYRING. This as-

sumes viscosity can be treated as a unimolecular reaction and reduces essentially to the equation

$$\eta = (hN/V) \exp[- S^*/R] \exp[U^*/RT] ,$$

where S^* is the entropy of activation and U^* the energy of activation for movement of a molecule from one position of equilibrium to another in the melt. If U^* is equated with E_η observed empirically from equation (1) (see however ([12])), it is then possible to compare the nominal values of S^* for liquids of different structure. Even though the theoretical assumptions may not be fully valid, S^* can be regarded as a structure index for the process of viscous flow (cf. also ([13])).

At present, this more theoretical approach involves assumptions (cf. references ([12,13])) which make it advisable to treat the trend in parameters of the melts, on approaching the freezing point, with reserve. Work in this direction is in train.

9. – Transport Mechanisms in Other Types of Melt.

9·1. *Heat transport and mass transport.* – At present, hardly any systematic investigations are available which deal specifically with heat transport near the freezing point. From some rather suggestive experiments ([14]), an enhanced heat transport in KNO_3 melts near the F.P. has been claimed. This has been attributed to the presence of « regions » of higher order and lower heat-content in these melts ([14]) near the freezing point. Related phenomena have also been observed for molten metals ([14,15]).

9·2. *Transport Phenomena in Ionic Melts near the Freezing Point.* – With regard to mass transport, anomalous diffusion effects should accompany anomalies in momentum transfer. In organic melts, the measurements are still too difficult to be rewarding. The use of labelled radioactive molecules may open up this field. In ionic melts, the possibility of using additional techniques of measurement has, however, permitted the investigation of structural effects in the liquids. Though the subject of ionic melts is too extensive for development in full detail, brief mention of the main features as at present known may serve to introduce some of the special problems of transport mechanisms in relation to structure.

An ionic melt consisting of spherically symmetrical ions must show very considerable order, because of the tendency for the $+ ve$ ion to be surrounded by $- ve$ neighbours, and vice versa. Melting points of ionic crystals are ge-

(12) P. F. VAN VELDEN: *Physica*, **13**, 529 (1947).
(13) A. BONDI: *J. Chem. Phys.*, **14**, 591 (1946).
(14) O. SCHAABER: *Zeits. f. Metallkunde*, **43**, 251 (1952).
(15) G. CARERI, A. PAOLETTI and F. L. SALVETTI: *Nuovo Cimento*, **11**, 399 (1954).

nerally so high, however, that practically no X-ray studies have yet been reported on the melts. Certain ionic crystals such as the nitrates melt at temperatures which are markedly lower. Here, there is some evidence of order ([16]) but the X-ray results are not yet very abundant.

Apart from this tendency to obtain ordered melts of spherically symmetrical ions, arising from the electrostatic forces, the structure of ionic melts should be closely similar to that of melts of the inert gases. These are almost certainly based on crystal lattices of close-packed spheres, extensively broken up by isolated and cooperative crystal defects. Passage from the crystal to the melt is in such cases accompanied by a substantial increase in volume, since most of the defects involve repulsion potentials higher than in the ordered crystal. (See Table IV.)

TABLE IV. – *Volume changes for spherically symmetrical units.*

Substance	$\Delta V_f/V_s$
NaCl	0.30
Neon	0.15
KCl	0.23
Argon	0.144

For all such « simple ionic melts », the migration of individual ions under the action of an external potential gradient requires less activation than the movement of ions involved in viscous flow in the melt. Such melts show two main transport characteristics.

(i) They follow the usual viscosity — temperature and fluidity — volume plots, giving good straight line relationships so far as is known ([17]).

(ii) The ratio E_η/E_σ of the activation energy for viscous flow to that for ionic migration under the influence of an electric field, is always greater than unity, since larger groups or clusters of ions are involved in viscous flow, than in ionic transport. This is illustrated in Table VI below.

10. – Ionic Crystals of Low Melting Point.

Classes of ionic crystals are known, which have melting points that appear to be exceptionally low, compared with similar electrostatic assemblies, composed of spherically symmetrical units. Some of the instances are quoted in Table V. ([16])

([16]) References in W. J. DAVIS, S. E. ROGERS and A. R. UBBELOHDE: *Proc. Roy. Soc.*, A 220, 14 (1953).

([17]) H. BLOOM and E. HEYMANN: *Proc. Roy. Soc.*, A **188**, 392 (1947).

On the basis of various investigations, the interpretation of these low melting points which is guiding our studies of them is that these melts show additional structural features, broadly described as « association complexes », which are not apparent to anything like the same extent in the ionic melts of spherically symmetrical ions. No final interpretation of the bond-origin of such association complexes need be attempted here. The main features

TABLE V. – *Melting points in relation to ionic symmetry M.P. °C.*

Anion \ Cation	Li	Na	K	Ag
Cl	614	800	770	455
I	446	651	723	552 *d*
ClO_3	124	250	386	230
NO_3	251	318	333	212
NO_2	< 100	271	387	140

for present discussion are as follows:

(i) Because the structure of the melt is more complex, contributions (ΔS complex) to the entropy of fusion can be provided additional to the usual entropy of disorder (ΔS disorder) without requiring large additions to the heat of fusion H_f. As a result, the freezing point $T_f = H_f\ (\Delta S_{\text{disorder}} + \Delta S_{\text{complex}})$ of melts containing association complexes of some kind is normally lower than that of simpler ionic melts which are otherwise similar.

(ii) In melts containing association complexes, the volume change on melting is less than for simple ionic melts, in which positional disorder can only be achieved at the expense of a considerable increase in volume. ([16])

(iii) Since either the anion or cation or both are present largely as association complexes, the ratio of the activation energy for ion transport to that for momentum transport, lies much nearer unity than for simple ionic melts. This is particularly true near the freezing points where association clusters predominate. (See Table VI.)

TABLE VI.

Cation	E_η/E_σ near M.P. NO_3'	E_η/E_σ near M.P. Cl'	E_η/E_σ well above F.P. NO_3'
Li	1.4	7.65	2.4
Na	1.2	6.1	1.8
K	1.2	3.4	1.6
Ag	1.4	5.3	—

As the temperature rises the clusters become smaller in size and fewer, and the ratio E_η/E_σ increases, thus tending more nearly to that for simple ionic melts such as the chlorides.

(iv) The $\lg \eta$ versus $1/T$ or the $1/\eta$ versus V plots may or may not show evidence of clustering. In the pure melts, this depends on what range of temperatures around and below the freezing point can be covered experimentally. By studying viscous flow and ion transport in mixed melts, this range of temperatures can be extended below the freezing point of the pure salt. In such mixed ionic melts, evidence of increased clustering on cooling has been observed (unpublished observations).

INTERVENTI E DISCUSSIONI

— G. CARERI:

Has the Einstein relation between mobility and diffusion been verified for the case of fused salts?

— A. R. UBBELOHDE:

I do not know of any test of the Einstein relation in the fused salts.

— A. CIMINO:

According to a recent paper by GREENWOOD and MARTIN there seems to be evidence of discontinuity at the melting point for supercooled liquids. Is it possible to show any evidence for embryo-formation by density measurements?

— A. R. UBBELOHDE:

The statistical method used to establish the deviation at the melting point is open to some question, from the standpoint of error theory. I do not believe the density to be more significant than the viscosity, however.

— P. G. BORDONI:

Did you employ a dynamical method in your viscosity measurements? Some years ago measurements of velocity and absorption of elastic waves were made by PETRALIA in the supercooled state.

— A. R. UBBELOHDE:

Our measurements were made by a flow method, using a capillary tube which involves only small rates of shear.

— H. C. Longuet-Higgins:

It may be of interest to quote some recent work on liquid crystals which Prof. Dewar has been doing at Queen Mary College, London, and which is to be published shortly. This work indicates that a substance A which forms a crystalline liquid mixture with a second substance B sometimes exhibits a latent transition point below the melting point. At this latent transition point the supercooled liquid A would be in equilibrium with a liquid crystal phase, and this suggests that there are different ways in which a liquid may become ordered by a cooperative mechanism. There is, in fact, no necessary connection between the phenomenon of freezing and the mutual orientation of molecules which is responsible for the formation of liquid crystals; and it would not be correct to ascribe the phenomenon of « pre-melting » to the formation of an intermediate liquid crystal phase.

— G. Careri:

Can Ubbelohde explain the difference between his clusters and the embryos introduced by Frenkel?

— A. R. Ubbelohde:

It is not necessary for the clusters to have the same structure as the crystal. It seems necessary to postulate their existence when there is an increase of the order inside the liquid, but arrangements with decreased entropy and volume can be formulated, which nevertheless do not have sufficient order to act as nuclei for crystal growth.

Transport Processes in Fluids.

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1. – Introduction.

This review of the theory of transport, and particularly of diffusion, in fluids, is written from the point of view of an interested observer rather than an active participant in the subject. For this reason the following remarks are necessarily superficial; and it has been impossible to give more than a sketch of the manner in which different physical ideas and models have been translated into mathematical terms. My main endeavour has been to evaluate and to compare from a physical viewpoint the different theories, more and less successful, which have been propounded from time to time to describe and to correlate different aspects of fluids transport phenomena, and to make some tentative suggestions as to how, in the absence of a complete theory, the experimentalist may set about interpreting new data of a quantitative kind. Some suggestions are also made at the end as to the sort of empirical questions whose investigation may be particularly helpful to those whose difficult task it is to correlate the macroscopic properties of fluids with their microscopic structure.

The problem of fluid transport may be approached on two distinct levels of enquiry. At the more empirical level one may enquire as to the connections between different transport processes and the corresponding phenomenological coefficients. On the other and more fundamental level one may attempt to establish mathematical relations between the transport coefficients and the intermolecular potentials. It seems safe to say that hitherto questions of the former kind have yielded more easily to investigation than those of the latter; and that while we have a good understanding of non-uniform gases from both points of view, a fully statistical theory of non-uniform liquids is not yet within our grasp, in spite of the magnificent pioneer work of KIRKWOOD and others. In this review, therefore, relatively little need be said about transport in gases, and more space will be devoted to liquids and to the outstanding theoretical and experimental questions about transport in the liquid phase.

2. – The Phenomenological Coefficients.

In single-component systems the most important transport phenomena are thermal conduction and viscous flow. Self-diffusion may also be considered to occur, but strictly speaking diffusion processes are only observable in two-component systems. The coefficients of thermal conductivity and viscosity are, of course, well defined only if the gradients of temperature and strain velocity are sufficiently small; otherwise the fluxes of energy and momentum are not proportional to these gradients. However, for nearly uniform mono-atomic fluids the thermal conductivity $\varkappa$, the viscosity η and the bulk viscosity η_b are functions only of the intermolecular forces, the molecular mass and the local temperature and density. In systems of more than one component other irreversible processes can occur, of which the most obvious is diffusion. In concentrated solutions diffusion will in general lead to the production of temperature gradients, and vice versa. However, if the components are very nearly identical this effect will be absent, for reasons which are physically obvious. Self-diffusion, which can be studied in isotopic mixtures, is therefore a simpler phenomenon than mutual diffusion, and may be thought of as occurring in systems which are virtually homogeneous. Furthermore, we may expect that Soret coefficients, which measure the coupling between diffusion and thermal conduction, will be closely connected with heats of mixing, since both vanish in isotopic mixtures. Other transport processes, such as electrolytic transport and chemical reaction, present more specialized problems and will not be discussed in this review.

Coefficients of thermal conductivity, viscosity and self-diffusion, and their dependence on temperature and density are, then, the basic raw material for the theory of fluid transport in one-component systems; if the molecules have no internal degrees of freedom, as in the inert elements such as argon, these three transport processes are in fact the only ones than can occur.

3. – The Thermodynamic Approach.

The extension of thermodynamics to non-equilibrium systems began with the work of ONSAGER in 1931. ONSAGER used the Gibbs equation

$$T\,\mathrm{d}S = \mathrm{d}E + p\,\mathrm{d}V - \sum \mu_\alpha \mathrm{d}n_\alpha\,,$$

to define the local entropy density in an anhomogeneous system, and demonstrated that the time derivative of the entropy density is a bilinear form in

the gradients X_i and the corresponding fluxes J_i:

$$\dot{S} = \sum_i J_i \cdot X_i .$$

In diffusion, for example, X represents the concentration gradient and J the relative flux of the two components, suitably defined. Assuming the so-called « linear laws » of transport, which are usually found to apply in the neighbourhood of equilibrium,

$$J_i = \sum_k L_{ik} X_k ,$$

he then showed, by an appeal to the principle of microscopic reversibility, that the « phenomenological coefficients » L_{ik} form a symmetric matrix, in the sense that

$$L_{ik} = L_{ki} .$$

(More precisely, $L_{ik}(H) = L_{ki}(-H)$, where H is any magnetic field). The diagonal coefficients L_{kk} are, in suitable units, none other than those of viscosity, thermal conductivity, diffusion, etc.; so Onsager's theory is particularly valuable in correlating the various coupling effects, such as the Soret effect, that can occur in non-equilibrium systems.

It is usually stated, and this is indeed the case, that Onsager's extension of thermodynamics merely gives relations between the transport coefficients L_{ik} and has nothing to say about their values in particular systems. Perhaps it should be mentioned here, however, that in his 1945 paper on liquid diffusion Onsager succeeded in deriving the classic relation

$$D = kT/6\pi a\eta ,$$

for the diffusion coefficient of a Brownian particle from the equations of non-equilibrium thermodynamics alone. It is true that he invoked Stokes' law for the force on a moving spherical particle, but this law follows from the equations of hydrodynamics, which themselves can be derived completely from Onsager's theory. This equation must therefore be regarded as one of the most soundly based relationships in the whole theory of transport phenomena. However, Stokes' law is only valid if the Brownian particle is much larger than the solvent molecules: so in order to calculate molecular coefficients of diffusion, thermal conduction and so on, it is necessary to use statistical models; and this is where the real mathematical difficulties begin.

4. – Statistical Theories of Transport.

The only type of fluid for which it is possible to calculate transport coefficients accurately from the intermolecular forces is the rarefied gas. The fundamental theoretical work in this field was done by ENSKOG, and the most comprehensive and authoritative account of the subject is undoubtedly the monograph by CHAPMAN and COWLING entitled *The Mathematical Theory of Non-Uniform Gases.* (An excellent exposition of the same theory is also to be found in the recent book by HIRSCHFELDER, CURTISS and BIRD: *The Molecular Theory of Gases and Liquids*).

The principal physical assumption underlying the theory is that on which Boltzmann's famous « H-theorem » is based, namely the « hypothesis of molecular chaos ». According to this hypothesis the probability of a given molecule becoming involved in a particular type of encounter with another molecule depends only on its instantaneous position and momentum, and not on its recent history. A mathematical consequence of this assumption is that the various fluxes of energy, momentum and matter may be obtained from the single-particle distribution function $f^{(1)}(r, p, t)$ and the intermolecular potentials, without reference to the many-particle distribution functions $f^{(n)}(r_1 ... r_n, p_1 ... p_n, t)$; these latter are accurately given by the superposition approximation for particles which are not in collision. The hypothesis of molecular chaos is embodied mathematically in Boltzmann's integro-differential equation for $f^{(1)}$ and ENSKOG solved this equation by a series expansion of $f^{(1)}$, in which the leading term corresponds to the Maxwell-Boltzmann solution for statistical equilibrium. For small departures from equilibrium the first correction to the Maxwell-Boltzmann distribution leads to fluxes which are linear in the gradients; and the achievement of ENSKOG consists in having obtained explicit expressions for the transport coefficients, in terms of the masses and laws of force between the particles. Furthermore, quantitative predictions based on Enskog's theory have been fully verified by measurement, at least in the range where classical statistical theory would be expected to hold.

The possibility of an exact mathematical theory of non-uniform gases appears to depend on the physical fact that energy and momentum are transported in a gas by « convection » — that is, by bodily movement of individual molecules through relatively large distances — and that the exchange of energy and momentum occurs almost entirely through bimolecular collisions, which are relatively infrequent events for a given molecule. In dense gases and liquids, on the other hand, a given molecule spends the greater part of its time interacting strongly with other molecules, and the very idea of a collision loses its significance. Furthermore, there is every reason to think that the mechanisms of heat conduction and viscous resistance are quite different

in a liquid and in a gas; not only is the temperature dependence of viscosity qualitatively different in the two cases, but whereas in a liquid diffusion is a slow process, the conduction of heat is rapid, indicating that the transport of thermal energy takes place not by molecular convection but by direct transfer between neighbouring molecules, like the members of a crowd pushing one another. For these reasons, if for no others, any complete theory of transport in liquids must incorporate certain essential features which are absent in the gas theory, and will inevitably be more complex mathematically. Before discussing recent theories of liquid transport, however, it will be appropriate to refer to two older theories which have a bearing on the problem. The first of these is Enskog's theory of dense gases, and the second the classical theory of Brownian movement.

5. – Transport in Dense Gases.

There is one type of dense fluid in which the idea of a collision retains an exact meaning, and that is a fluid composed of hard non-attracting spheres. It might be expected, furthermore, that the inert gases at high temperatures and pressures might be fairly well represented by such a hard-sphere model, since in comparison with the repulsive forces the attractive forces are small and vary rather slowly with distance. Now from purely dimensional arguments it is possible to draw some important conclusions about the dependence of the transport coefficients of a hard-sphere fluid on temperature and density and molecular mass. If m, l, t and T represent the dimensions of mass, length, time and temperature respectively, then the transport coefficients for viscosity, thermal conduction and diffusion have the respective dimensions:

$$\begin{aligned} \eta &= m\cdot l^{-1}\cdot t^{-1} \\ \varkappa &= m\cdot l\cdot t^{-3}\cdot T^{-1} \\ D &= l^2\cdot t^{-1}\,. \end{aligned}$$

The fact that temperature has the dimensions $k^{-1}\cdot m\cdot l^2\cdot t^{-2}$ makes it possible to eliminate the time dimension from the transport coefficients and write them as:

$$\begin{aligned} \eta &= m^{\frac{1}{2}}\cdot l^{-2}\cdot k^{\frac{1}{2}}\cdot T^{\frac{1}{2}} \\ \varkappa &= m^{-\frac{1}{2}}\cdot l\cdot k\cdot T^{\frac{1}{2}} \\ D &= m^{-\frac{1}{2}}\cdot l\cdot k^{\frac{1}{2}}\cdot T^{\frac{1}{2}}\,. \end{aligned}$$

These equations show how the transport coefficients will vary with molecular mass, size and temperature for a given ratio of the molecular volume to that of the container. In particular, for a given density, all the transport coefficients

should vary directly as the square root of the temperature. As far as the viscosity is concerned, this conclusion appears to be in flagrant contradiction with the fact that liquid viscosities usually decrease exponentially as the temperature rises; and diffusion coefficients normally show an exponential, rather than a square root, dependence on temperature. However, measurements of these coefficients are normally made at constant pressure rather than at constant density, and it is therefore of crucial importance to know *a*) how sensitive the transport coefficients are to the fraction of space occupied by the spheres and *b*) how in an experimental project one is to estimate this fraction. ENSKOG has given a quantitative answer to the first question, and has shown that at high densities, as might be expected, the coefficients of viscosity and diffusion are very sensitive functions of density. Enskog's final formulae for a gas of rigid spherical molecules are:

$$\frac{\eta v}{\eta_0 b} = \frac{1}{y} + 0.8 + 0.761y\ ,$$

$$\frac{\varkappa v}{\varkappa_0 b} = \frac{1}{y} + 1.2 + 0.755y\ ,$$

$$\frac{Dv}{D_0 b} = \frac{1}{y}\ .$$

Here η_0, $\varkappa_0$, D_0 denote the zero-pressure values of the viscosity, thermal conductivity and self-diffusion coefficient; b denotes the volume of one of the molecules multiplied by 4; v denotes the volume of the container per molecule, and y denotes the quantity $pv/kT - 1$. ENSKOG suggests that in applying these equations to real substances one should regard b as a parameter adjusted to fit the minimum in the viscosity curve, and should replace p by the « thermal pressure » $T(\mathrm{d}p/\mathrm{d}T)_v$, evaluated from the equation of state. (For hard-sphere fluids the last named quantities may easily be shown to be equal). On the basis of these suggestions he succeeds in disposing of the apparent contradiction and in obtaining a reasonably successful quantitative theory of the transport coefficients of gases at high densities (see, for example, the book by HIRSCHFELDER and others, already referred to).

The most important point arising from these rudimentary considerations is that one may expect transport coefficients to vary with temperature in ways which are completely different at constant density and at constant external pressure. That this is so has been demonstrated experimentally by BRIDGMAN (1931), who found that non-polar liquids have small temperature coefficients of viscosity *at constant volume*; the variation of viscosity with temperature at constant pressure would therefore appear to arise mainly from thermal expansion.

6. – The Theory of Brownian Motion.

We now proceed to a discussion of the classical theory of Brownian motion, since this theory has provided the inspiration for what is probably the most promising modern theory of transport in liquids, namely that of KIRKWOOD and his collaborators. According to the Brownian theory, with which are associated the names of EINSTEIN and SMOLUCHOWSKI, a colloidal particle suspended in a liquid may be thought of as subject, on the one hand, to random accelerations due to bombardment by individual molecules of the liquid, and on the other hand, to a steady deceleration due to viscous forces. This division of the forces on the particle into those of microscopic and those of macroscopic origin is difficult if not impossible to justify rigorously; but it constitutes the essential feature of the theory, and makes a strong appeal to our physical intuition.

The following account is based on the masterly review by CHANDRASEKHAR (1943), and is intended to do no more than sketch the background of ideas on which Kirkwood's theory is based.

A colloidal particle is assumed to satisfy Langevin's equation of motion, namely

$$\frac{\mathrm{d}u}{\mathrm{d}t} = A(t) - \beta u \ ,$$

where $A(t)$ is a rapidly fluctuating force due to molecular bombardment, and $-\beta u$ is the dynamic friction experienced by the particle. Two assumptions are made concerning $A(t)$: first, it is assumed independent of the position and velocity of the particle, and secondly it is assumed to fluctuate with a frequency which is large compared to β^{-1}. These assumptions seem slender for the construction of a quantitative theory, but they suffice if use is made of the fact that the distribution of particle velocities in equilibrium is Maxwellian. If we denote by $w(u, t; u_0)$ the probability that a particle with velocity u_0 at $t = 0$ has attained a velocity u at time t, then the Maxwell distribution demands that

$$\lim_{t\to\infty} \{w(u, t; u_0)\} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left[\frac{-m|u|^2}{2kT}\right] .$$

If this condition is imposed, it can be demonstrated that if t is much greater than β^{-1}, the probability that a particle which started from r_0 with a velocity u_0 has reached a point r at time t is

$$w(r, t; r_0, u_0) = \left(\frac{1}{4\pi Dt}\right)^{\frac{3}{2}} \exp\left[\frac{-|r - r_0|^2}{4Dt}\right] ,$$

where $D = kT/m\beta$. But for a spherical particle of radius a,

$$m\beta = 6\pi a\eta ,$$

where η is the viscosity of the medium. It follows that the quantity D, to be identified with the diffusion coefficient, is related to the viscosity by the simple equation

$$D = \frac{kT}{6\pi a\eta} .$$

If we now regard the function $w(r, t)$, or the more complete function $w(r, u, t)$ as probability distributions in position space or position-velocity space, it is possible to derive from the theory differential equations which govern the time-development of these probability distributions. (The derivation of these equations is of great mathematical elegance, but unfortunately there is not space to give it here). The differential equation for $w(r, u, t)$, known as the Fokker-Planck equation, may be written in the form

$$\frac{\partial w(r, u, t)}{\partial t} + u \cdot \nabla_r w = \beta \nabla_u (wu) + \frac{kT\beta}{m} \nabla_u^2 w ,$$

if no external forces are acting. (If a gravitational or other acceleration K is present, a term $K \cdot \nabla_u w$ must be added to the left hand side). If, as often happens, we are interested only in intervals of time which are long compared to β^{-1}, then the velocity at the end of such an interval will be uncorrelated with its value at the beginning, and we may ignore the velocity distribution altogether. The resulting differential equation for $w(r, t)$, in the presence of an external acceleration K, is called Smoluchowski's equation, and takes the form

$$\frac{\partial w(r, t)}{\partial t} = \nabla_r \left(\frac{kT}{m\beta} \nabla_r w - \frac{K}{\beta} w \right) .$$

In the absence of external forces, Smoluchowski's equation reduces at once to the simpler « diffusion equation »

$$\frac{\partial w}{\partial t} = \frac{kT}{m\beta} \nabla^2 w ,$$

showing that the quantity D is indeed the diffusion coefficient.

The extreme simplicity of this theory, the economy of its assumptions, and above all the fact that it accounts simply for the fundamental irreversibility of diffusion phenomena (the diffusion equation being first order in the time),

make it a very attractive starting point for more general statistical theories, and in the following paragraphs we shall attempt to show how some of its fundamental concepts have been incorporated into such theories.

7. – The Statistical Theory of Transport in Liquids.

The most interesting and promising general theory of transport processes in liquids is that of KIRKWOOD and his collaborators, expounded in a series of papers in the *Journal of Chemical Physics*, dating from 1946. A good review of this theory is to be found in a paper by EISENSCHITZ (1952).

In principle, as KIRKWOOD observed, the complete motion of a classical fluid is determined by the Liouville equation, which is a differential equation determining the time-variation of the distribution function $f^{(N)}(r_1, ..., r_N, p_1, ..., p_N; t)$. This function specifies the probability that the coordinates and momenta of all the particles have specified values at a given moment, and the Liouville equation determines the flow of probability in phase space. The equation may be written in the vector form

$$\frac{\partial f^{(N)}}{\partial t} + \sum_k \left\{ \frac{p_k}{m} \cdot \nabla_{q_k} f^{(N)} + F_k \cdot \nabla_{p_k} f^{(N)} \right\} = 0 ,$$

or, more concisely,

$$\frac{Df^{(N)}}{Dt} = 0 ,$$

where D/Dt represents the hydrodynamic time derivative in phase space. The form of the Liouville equation, however, shows at once that it is reversible in the time, whereas irreversibility is an essential characteristic of transport processes, which are dissipative in nature. Hence, even were it possible to solve the equation exactly, the solution would throw no immediate light on these processes.

In practice, however, one is only interested in a limited region of the fluid. Hence it is desirable to work with distribution functions of lower order, obtained by averaging over the coordinates and momenta of all but a small number, n, of molecules. This averaging process cannot be performed with complete precision, but KIRKWOOD has shown that it can be done, and leads to irreversible behaviour, if certain plausible assumptions are accepted. The most important of these assumptions concerns the existence of a small interval of time τ, long compared to the fluctuations of force on a molecole, but small compared to relaxation times; the mean force acting on a molecule is then taken as the average force over this short interval τ. In this manner KIRKWOOD

obtains an equation of the Langevin type governing the self-diffusion of an individual molecule, namely

$$\frac{\partial p_1}{\partial t} = (F_1 - \bar{F}_1) - \frac{p_1}{3mkT}\int_0^\tau F_1(0)\cdot F_1(t)\,\mathrm{d}t = G_1 - \beta p_1\,,$$

where F_1 is the instantaneous force due to all the other molecules and a bar denotes an average over the coordinates and momenta of all the other molecules. The validity of this equation depends on the assumption that the integral defining β attains a « plateau value » independent of τ if τ is not too small and not too large; and KIRKWOOD uses physical plausibility arguments to support this contention. The subsequent analysis follows exactly the lines of the theory of Brownian movement; so the self-diffusion coefficient of a liquid is seen to depend entirely on the autocorrelation in time of the instantaneous force acting on a molecule, this autocorrelation decaying to zero after an interval τ.

In a similar manner the viscosity and thermal conductivity can be calculated when one knows the distribution function for the coordinates and momenta of a pair of molecules. This function depends, of course, on the relative coordinates and momenta; and it can be shown to satisfy an equation of the Fokker-Planck type, involving another friction constant γ, defined as

$$\gamma = \frac{1}{3mkT}\int_0^\tau F_2(0)\cdot F_2(t)\,\mathrm{d}t\,,$$

where F_2 denotes the instantaneous force on one of the molecules, excluding that part which is due to the other. This Fokker-Planck equation may be reduced to a Smoluchowski equation involving only the distribution function for the relative coordinates — the so-called radial distribution function, and this equation must then be solved subject to appropriate boundary conditions or the function evaluated by some other means. There are some uncertainties as to the correct boundary conditions; KIRKWOOD, BUFF, and GREEN, using one set of conditions, have succeeded in calculating the viscosity of liquid argon within a factor of 2, but EISENSCHITZ and SUDDABY have proposed alternative conditions which spoil this agreement. The latter authors suggest, however, that the agreement was misleading in that KIRKWOOD and his colleagues had assumed an exponential decay of the force correlation, whereas this decay may well have an oscillatory character due to the partially vibrational character of the molecular motions.

It seems fair to say of Kirkwood's theory that at present, therefore, it does not lend itself to the quantitative calculation of transport coefficients

without the aid of dubious extra assumptions; but the underlying ideas seem to be correct, and we may hope that the various technical obstacles may be overcome in the not too distant future.

Before leaving the subject of absolute statistical theories of transport, reference should perhaps be made to two other theories, that of BORN and GREEN and that of EYRING. Little, unfortunately, can be said about the former without going into mathematical technicalities; but the theory of BORN and GREEN is in the same spirit as that of KIRKWOOD, and uses a similar type of superposition approximation to reduce distribution functions of high order to those of lower order. However, the application of the theory demands the solution of non-linear integro-differential equations, and the linearization of these is a drastic approximation whose validity it is virtually impossible to assess in the absence of any understanding of the physical assumptions implied by the approximation. It is perhaps not therefore surprising that the theory of Born and Green has hitherto been unfruitful in relation of experiment.

Eyring's theory of liquids differs from those just described in that it is based upon a rough physical model rather than on sophisticated mathematical approximations. For this reason, in Onsager's words, the method « lends itself to a facile interchange of deduction and induction »; but this practical advantage is offset by the difficulty of using it for fully absolute calculations. HIRSCHFELDER, STEVENSON and EYRING (1937) picture the elementary step in diffusion as the jumping of a single molecule from one equilibrium position to another, and find the coefficients of viscosity and diffusion to be related by the equation

$$kT/D\eta = a_1 a_2/a_3 ,$$

where a_1, a_2 and a_3 are lengths of molecular dimensions. The experimental results can indeed be fitted by such an equation with not unreasonable values of the parameters; but they can also be fitted quite well by the equation of Brownian motion

$$kT/D\eta = 6\pi a ,$$

where a is the molecular radius. It would of course be naive to suppose that the theory of Brownian motion properly applies to the motion of an individual molecule, and indeed the value of a which fits the above equation is normally rather less than the molecular radius; but Eyring's theory is equally an approximation to the truth, and until it becomes possible to estimate the parameters a_1, a_2 and a_3 theoretically, it will be difficult to assess objectively the relative merits of the two theories as they apply to diffusion.

8. – The Present Outlook.

In so far as the above account is a fair analysis of the present theoretical position, one must reluctantly accept the fact that we have at present no statistical theory of transport in liquids which is at the same time absolute, practically useful and free from mathematical uncertainty. In the circumstances the experimentalist is faced with two important questions: how is he to interpret theoretically his experimental results, and what sorts of experimental data will be most valuable in the construction of future theories of transport? It would of course be rash to attempt to answer either of these questions more than tentatively; the following suggestions are intended merely as a basis for discussion.

It is an axiom of scientific investigation that one tests the simplest theory first. The simplest theory of diffusion which correlates *directly* measurable quantities is that of the Brownian motion of a spherical particle. Granted, the radius of a molecule is not precisely defined, but we can fix it within quite narrow limits and the predictions of the theory are correspondingly precise. Does the theory break down completely for particles of molecular size? According to the available evidence, the theory only loses accuracy, and still gives a correct order of magnitude for D; but further experimental evidence would be desirable.

An outstanding theoretical question is the relation between D and η. The simpler theories, as we have seen, suggest an intimate connection between them; on the other hand, they depend on different friction constants in Kirkwood's theory, and often show a different temperature dependence at constant pressure. It would be very valuable to have some more comparative data on D and η as functions of temperature, so that one could see how the « apparent molecular radius » varies with temperature. Particularly suitable substances for study would be the rare gases, whose molecules are truly spherical and of known size.

A related question is that of the effect of pressure or, more properly, of increasing density on the transport coefficients. If viscosity coefficients are very sensitive to density, is the same true of diffusion coefficients? One would imagine so, but very few data are available. Measurements at constant density over a range of temperature are of course rather difficult; but even measurements at constant pressure are valuable if accompanied by measurements of thermal expansion coefficients, compressibilities, etc.. It is quite possible that there may be a connection between compressibility and viscosity — both quantities represent measures of molecular « congestion ».

As to the future of the statistical theories themselves, it is both unwise and unhelpful to speculate. « Wovon man nicht sprechen kann, darüber muß man schweigen ».

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INTERVENTI E DISCUSSIONI

G. BORDONI:

The first derivative with respect to the time which occurs in the equation of the diffusion problems, shows that one cannot speak of a velocity of propagation. This

feature comes from the macroscopic picture of the continuum, but it is not much convenient in microphysics. CATTANEO has recently shown that a better approximation in the molecular theory of heat conduction in gases gives rise to a velocity of propagation of the same order as the thermal velocity of molecules.

— H. C. LONGUET-HIGGINS:

The theory of stochastic processes makes it clear, I think, why the first time derivative appears in the diffusion equation. The reason is that the production of entropy depends upon a succession of uncorrelated events which in the cases considered are the exchange of energy or momentum or position between different pairs of molecules. The only cases in which the second time derivative appears are those in which the process is either reversible, as in the transmission of sound through a gas, or « pseudo-reversible » as in the propagation of thermal energy through a chain of harmonic oscillators. PEIERLS showed that the latter phenomenon is governed not by the diffusion equation but by the wave equation, and this is essentially because there is no mechanism for the scattering of phonons in a harmonic lattice. Another « pseudo-reversible » process is the transmission of « second sound » in liquid helium. The equation of propagation in this case takes an unusual form because of the absence of momentum exchange between the ordinary fluid and the superfluid, as shown by the work of PRIGOGINE and MAZUR.

— A. R. UBBELOHDE:

The internal degrees of freedom play an important part, and one would expec. the viscosity to depend from molecular complexity, especially for flexible moleculest

— G. CARERI:

BORN and GREEN derived an approximate expression for the viscosity coefficient, where the exponential dependence from the temperature is well evident. However, the activation energy is very low in these processes.

Sul secondo coefficiente di viscosità dei liquidi.

A. Carrelli

Istituto di Fisica dell'Università - Napoli

Due articoli particolareggiati sui risultati ottenuti, in questo argomento, per l'acqua l'alcool amilico, il benzolo e il tetracloruro di carbonio sono già apparsi nel *Nuovo Cimento*, **11**, 429 (1954) e **12**, 1 (1954).

Nuclear Relaxation and Quasi-Crystalline Structure of Liquids.

G. Chiarotti, G. Cristiani and L. Giulotto

Istituto di Fisica dell'Università - Pavia

Some results on nuclear relaxation in pure liquids are reported. In some cases the thermal relaxation time seems to be somewhat longer than we can expect from the theory of Bloembergen and coworkers. The observed discrepancies could be due to a quasi-crystalline structure of liquids.

A detailed report on the obtained results for pure liquids and liquids containing paramagnetic gases in solution will soon appear in the issue of May of *Il Nuovo Cimento*, 1955.

Tangential Modulus in Some Metals near the Melting Point.

P. G. BORDONI and M. NUOVO

Istituto Nazionale di Ultracustica - Roma

In a previous investigation (1), the temperature changes of phase velocity have already been measured for extensional waves in some metals (Sn, Pb, Bi, Al, Cd) near their melting point. It was found, that even at those temperature, the Young modulus, which is proportional to the square of velocity,

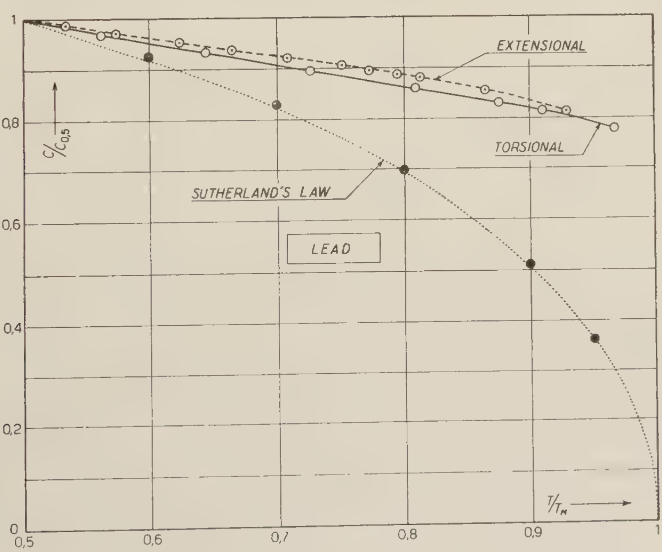

Fig. 1

has comparatively large values, and undergoes a sudden decrease in a very small temperature range during the melting process.

(1) P. G. BORDONI and M. NUOVO: *Nuovo Cimento*, **10**, 386 (1953); *Ric. Scient.*, **23**, 593 (1953).

The experimental technique ([2]) has been recently improved ([3]), and it is now possible to measure also the torsional velocity, whose square is proportional to the second Lamé's constant. In order to complete our knowledge of the elastic behaviour of solids at high temperatures, a new investigation was therefore started, to determine the temperature changes of the tangential modulus near the melting point. Measurements have been already carried out on tin, lead and bismuth, and are presently in progress on aluminium and cadmium.

The aim of the present note is to present a few preliminary remarks on

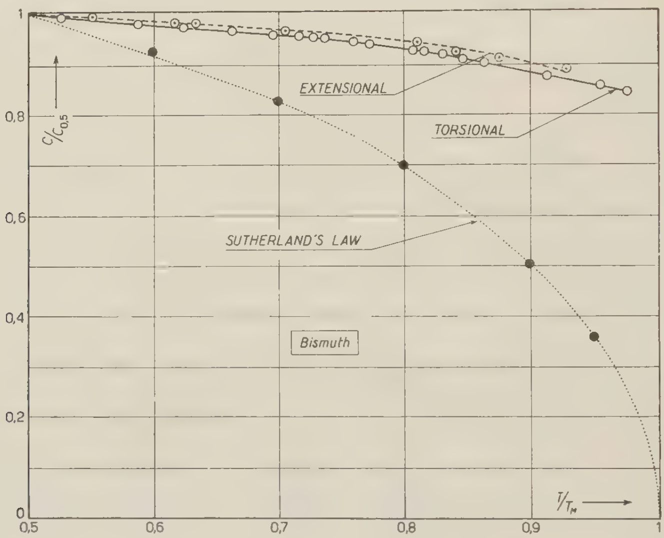

Fig. 2-

the results already obtained, while a complete analysis of all experimental data will be given in a following paper.

It may be observed that the modulus *vs.* temperature curves in all metals in which measurements were made exhibit a very similar behaviour both in the extensional and tangential case, as it is shown for lead in Fig. 1. To make comparisons easier the curves do not give the absolute values of velocity c, but their ratios to the velocity $C_{0,5}$, measured at half the melting point temperature. For the same reason the ratios of absolute temperature T to the melting value T_M have been taken as abscissae. In addition to the new experimental data on torsional velocity, the old ones concerning extensional waves have been plotted on the same diagram, together with the theoretical curve

([2]) P. G. Bordoni: *Nuovo Cimento*, **4**, 177 (1947); *Ric. Scient.*, **18**, 103 (1948).
([3]) P. G. Bordoni and M. Nuovo: *Comptes Rendus du Congrès d'Éléctroacoustique*, Delft, Juin 1953, p. 184; *Ric. Scient.*, **24**, 560 (1954).

which gives the changes in torsional velocity according to Sutherland's law for the tangential modulus.

The experimental curve for lead, and the analogous ones for bismuth (Fig. 2) and tin (Fig. 3), show that the torsional velocity does not go to zero, when temperature approaches the melting point, in contrast with Sutherland's hypothesis. As the temperature coefficient of velocity increases slightly with temperature (*), it is easily seen from the experimental curves that even at temperatures as high as $0.97\,T_M$ the torsional velocity is always larger than one half of its value at absolute zero. The agreement that L. BRILLOUIN

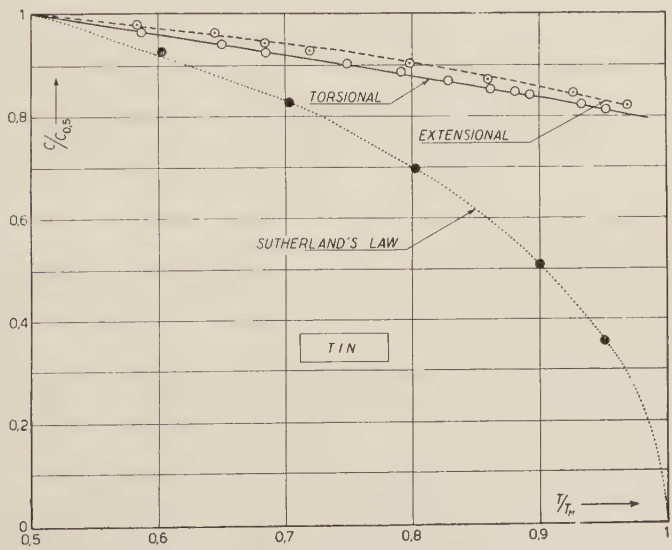

Fig. 3.

pretends to find between Sutherland's law and some experimental data [6] is probably due to the errors which necessarily affect the static measurements of the modulus at high temperatures, owing to anelastic strain, and to relaxation phenomena. As it was already pointed out [7] these errors can be made quite negligible in dynamic measurements, employing extremely small stresses and frequencies of vibration in the ultrasonic range.

The sudden decrease, which according to Figs. 1, 2 and 3, the tangential modulus undergoes during the melting process in a temperature range not

(*) This is true even at temperature lower than $0.5\,T_M$. It has also been shown [4,5] that near the absolute zero, the temperature coefficient varies like T^3.

(4) P. G. BORDONI: *Nuovo Cimento*, **10**, 268 (1953).

(5) P. G. BORDONI: *J.A.S.A.*, **26**, 495 (1954); *Ric. Scient.*, **23**, 1193 (1953).

(6) L. BRILLOUIN: *Influence de la température sur l'élasticité d'un solide* (Paris, 1940).

(7) P. G. BORDONI: *Atti del II Convegno Nazionale di Metallurgia*, Milano, 1948.

larger than $0.03 T_M$, seems to agree quite well with the structural theory which reduces melting to the instability of the crystal lattice.

INTERVENTI E DISCUSSIONI

— A. CARRELLI:

Quale è stato il metodo sperimentale adoperato?

— P. G. BORDONI:

Quello di eccitazione elettrostatica delle vibrazioni e di rilevamento pure elettrostatico a modulazione di frequenza, descritto alcuni anni or sono sul *Nuovo Cimento*, e già applicato in molte altre ricerche dello stesso tipo. Per la misura della velocità di propagazione delle onde torsionali ci si è valsi di alcuni perfezionamenti recenti dello stesso metodo, dei quali è stata data comunicazione al Congresso di Elettroacustica di Delft del 1953.

— A. R. UBBELOHDE:

BORDONI's results are in agreement with specific heat measurements.

— G. CARERI:

HUNTER and SIEGEL have investigated with a similar result the elastic constants of sodium near the melting point.

— P. G. BORDONI:

It is very difficult to decide whether it is better to make experiments on single crystals or on policrystalline aggregates. Obviously the results concerning single crystals are more fundamental. However this does not seem to be very important as far as the melting process is concerned. In fact the temperature of melting is not structure-sensitive. Probably the best procedure is to make a preliminary investigation on aggregates, and to clear doubtful points by means of measurements on single crystals.

— A. R. UBBELOHDE:

One must keep in mind that monocrystals have also a mosaic structure.

Tentative on the Rôle of Exchange Forces in the Problem of He II.

S. FRANCHETTI

Istituto di Fisica dell'Università - Firenze

Exchange forces were first considered in connection with He II by BIJL, DE BOER and MICHELS (*Physica*, 8, 655 (1941)). Here the subject is examined over again in some more detail.

To write down exchange integrals, one-particle eigenfunctions are built up showing an excess kinetic energy (with respect to the fundamental state) which is quadratically dependent on momentum. These eigenfunctions are thus not appropriate for describing phonons (i.e. the excitations characteristic of very low temperatures) but might instead usefully replace rotons, i.e. the excitations dominating over, say, 1 °K.

Only one arbitrary parameter is introduced and it turns out that it can be chosen so as to give the right amount of zero-point energy and at the same time an effective mass of the order of m_{He} (somewhat larger).

The exchange integrals are then studied and it turns out that the essential difference in respect of the case of free particles is the appearance of a *structure factor*, determined by the «local» eigenfunctions describing the motion of any atom in the average field of its neighbours.

These integrals contain a parameter to be fixed, namely a lower limit r_0 in the integration over the mutual distance of the interacting atoms.

To have an idea of what r_0 should be, the amount of heat absorbed is put in relation with the number of evaporated «particles» in the interval of temperature from 0 °K to the λ-point. The experimental data utilizd are those on the density ϱ_n of the normal fluid and those on specific heat. To get from them the energy $\mathcal{E}$ absorbed per evaporated particle, one needs an assumption as to the nature of the «particles». Two hypotheses are put to test: *a*) particles are phonons; *b*) particles are of atomic mass. The plot of $\mathcal{E}$ as a function

of T shows that reasonable results are obtained below 0.3 °K from assumption *a*) only, and above 0.8 °K from assumption *b*) only. (Neither, alone, is good in the intermediate region). This result offers a striking confirmation of the known fact that at low temperatures the excitations are linear in momentum, whereas at higher temperatures quadratic ones dominate. The importance of the $\mathcal{E}$ versus T diagram in the present connection lies however in the fact that it does not show the existence of any large excitation energy (not for instance of the kind generally postulated for rotons). Since exchange forces should give rise to an excitation energy (it can be shown that the exchange integrals must be non-negative, at least in the limit of zero momentum) the above result suggests that the unknown parameter r_0 should be so chosen as to give a practically zero value to the exchange integral in the limit of zero momentum (that is for $T \to 0$).

This can be achieved, since the value of the integral is a balance between a positive term and a negative one arising respectively from repulsive and attractive forces (*) and leads to a value of about 2 Å for r_0.

Now it so happens that this balance cannot be maintained as the temperature rises (and with it the momentum of the evaporated particles), the integrals shifting to larger and larger positive values. It is suggested that to avoid this increase of the energy, the local motion of the atoms arranges so that, through the play of the structure factor, the average value of the exchange integrals stays small. The *negative expansion* that takes place between about 1 °K and the λ-point should be a consequence of this rearrangement (in fact, a slight contraction of the local eigenfunctions).

To test somehow the above conclusion, the exchange energy, or, better, what this energy would be in the absence of any counteracting mechanism, has been calculated as a function of T and the curve compared with that of the density increase. The two curves show indeed good agreement.

A full account of the present work will be published elsewhere.

(*) The potential of Slater and Kirkwood has been used (*Phys. Rev.*, 37, 682 (1931)).

Self-Diffusion in Liquid Metals (*).

G. CARERI and A. PAOLETTI

Istituto di Fisica dell'Università - Roma

This communication is intended to report briefly some measurements of the self diffusion coefficient in liquid metals, and to discuss particularly the results on the basis of current theories of the liquid state. In fact, because of the continued insistence with which quasi-crystalline theories of liquids are put forward, we have carried out measurements for liquids already studied in the crystalline state, to enable a liquid-crystal comparison to be made.

At the present moment three metals, indium, tin and lead, have been examined; in each case the relation between the diffusion coefficient and the temperature has been found to be of the Arrhenius type

$$D = D_0 \exp[-E_D/RT]\,. \tag{1}$$

We do not want to enter into technical details about these measurements here. The results are shown in Table I, which also includes the data concerning liquid mercury, obtained recently by HOFFMANN with a different technique in the temperature range 0-90 °C. In our case instead, it was possible to go several hundred degrees above the melting point. In the absence of data for the noble elements in the liquid state, these are the only data concerning sufficiently monoatomic liquids.

It is natural to try to correlate the values of E_D with other important quantities for the liquid phase. No simple correlation exists between E_D and other quantities such as the melting temperature, latent heat of fusion, the latent heat of evaporation, the distance and number of the neighbouring atoms surrounding an atom in the liquid phase. There is no correlation between the energy of activation E_D of self diffusion and the analogous energy of activation

(*) For sake of briefness, no references have been quoted here. Full account will be given in a forthcoming paper under the same title.

TABLE I.

	T_m °K	Self-Diffusion				Viscosity	
		Crystal		Liquid			
		D_0	E_D	$D_0 \cdot 10^4$	E_D	$\eta_0 \cdot 10^3$	E_η
Hg	234	—	—	1.26	1160	5.55	600
In	429	1.02	17900	1.76	1350	3.85	1380
Sn	505	$3.7 \cdot 10^{-8}$ $1.2 \cdot 10^{-5}$	5900 10500 19000	12.4	3900	4.13	1603
Pb	601	6.60	27900	70	6000	4.08	2300

E_η for the viscosity; this is of some importance for what we shall say later. The strict similarity of behaviour of tin and lead seems to be traceable to the fact that tin and lead are neighbouring elements in the same sub-group of the periodic system, and so the movement of the metallic ions in the body of the liquid occurs in rather similar conditions.

We pass now to solid-liquid comparison in relation to the self diffusion coefficient. The values of D_0 and E_D for the crystalline metal are also included in Table I. Without taking into account the Fensham's values for solid tin, the comparison between liquid and crystal can be summarized as follows:

$$\frac{D_{0\,\text{liquid}}}{D_{0\,\text{solid}}} \approx 10^{-4} \div 10^{-3}\,, \qquad \frac{E_{D\,\text{liquid}}}{E_{D\,\text{solid}}} \approx 2 \cdot 10^{-1}\,. \tag{2}$$

As was said before, of the various attempts made up to the present to describe the behaviour of liquids, only those based on quasi-crystalline approximations have led to concrete expressions for the diffusion coefficient in simple liquids. The first application of the quasi-crystalline method to transport phenomena in liquids is due to FRENKEL in 1926. Both for a liquid and for a solid the movement of an atom is described as a succession of jumps from one position of equilibrium to another in the body of the crystal or pseudo-crystal. Using an analogous model Eyring and colleagues have deduced the viscosity and diffusion coefficients, η and D, of a simple liquid in a more correct manner. As usual the energy of activation is supposed to be, as for a solid crystal, the energy necessary in part to form a vacancy and in lesser part to make it move. It is possible to combine the expressions for the viscosity and the diffusion in such a way as to eliminate the quantity most difficult to cal-

culate, which is the frequency of the jumps, obtaining simply

$$D = \frac{KT}{2r\eta}, \tag{3}$$

where r is a length very near to the atomic radius. Formula (3) is interesting because the calculation contains no approximations, but is plausibly based on a model of a liquid which consists of holes.

It is now possible to check (3) using the data of Table I. It is obvious that this expression cannot be verified analytically because the activation energies for the viscosity and diffusion are not correlated as (3) would require. Furthermore, if the value of r is calculated, it is found to vary with the temperature and to be always excessively large (see Table II). Table II also shows

TABLE II.

Element	Metallic Radii PAULING	Calculated Radii		
		T °K	EYRING	EINSTEIN
Hg	1.57	234	7.32	0.77
		630	9.05	0.96
In	1.67	429	4.45	0.47
		1 000	9.92	1.05
Sn	1.58	505	7.45	0.79
		1 000	4.56	0.48
Pb	1.75	601	3.79	0.40
		1 000	3.53	0.37

the value of the atomic radius which would be found using the Stokes-Einstein formula. This formula is obviously deduced for conditions which certainly are not obtainable, i.e. those relative to the movement of a small sphere in a continuous viscous medium

$$D = \frac{KT}{6\pi r\eta}. \tag{4}$$

The resulting radii are too small, but always nearer to the actual ones than those furnished by Eyring's expression. In view of Kirkwood's work this fact deserves to be noted.

It is already evident from (3) that the quasi-crystalline model of a liquid is not suitable for the description of these transport phenomena. But more generally if Zener's expression for the diffusion coefficient in a crystal

$$D = \gamma \delta^2 \nu \exp [\Delta S/R] \exp [-(E_v + E_m)/RT] \tag{5}$$

is examined, it is seen that an expression of this kind cannot be suitable for a liquid metal. In fact, bearing in mind the liquid-crystal comparison by (2) it is seen that even admitting that all the holes are formed at the moment of melting, it does not seem possible that E_m should be so small in the liquid, neither can the smallness of the pre-exponential factor be accounted for.

In conclusion, these first data on diffusion in liquid metals show the difference between the known mechanism of the movement of the atoms in the solid phase, and that still ill-defined in the liquid phase.

INTERVENTI E DISCUSSIONI

— H. C. Longuet-Higgins:

In view of the great difficulty of applying Kirkwood's theory in its present form to particular fluids it is gratifying to see that Dr. Careri's results can be interpreted reasonably well by the Einstein theory, with a molecular radius of the right order of magnitude. The theory of Eyring is quantitatively inadequate, though it may contain an element of qualitative truth if one interprets the « holes » as local fluctuations in density.

— F. Seitz:

One can explain the low values of D_0 if one postulates E to be a function of the temperature, due to the greater thermal expansion of the liquids.

— A. R. Ubbelohde:

E will presumably also be a function of the specific volume of the liquid. If the thermal expansion of the liquid could be attributed solely to an increase in content of holes, without much increase in average separations of the molecules, E should not depend much on temperature. But temperature rises, and thus E decreases.

— F. G. Fumi:

Radiation damage experiments and theoretical estimates have shown that there exist in solid metals migration processes with activation energies as low as 0.1 eV, roughly of the magnitude of the activation energies that Careri reports for self-diffusion in liquid metals. These migration processes of low activation energy in solids, are thought to be associated with interstitials and vacancy clusters. It should also be noted that a factor of the order of $10^2 \div 10^3$ may be contributed to the D_0 for self-diffusion in solid metals by the entropies of formation and migration of defects. In

the transition from the solid to the liquid phase one should also expect a reduction in the frequency ν which appears in the expression of D_0.

Concerning the temperature dependence of the viscosity η, I should like to call attention to the recent work of ANDRADE who claims that for liquids such as the liquid alkali metals this dependence is expressed better by the law $\eta v^{\frac{1}{3}} = C \exp [c/vT]$, ($v$, specific volume), than by a simple exponential, $\eta = B \exp [b/T]$.

— G. BOATO:

Some unpublished work of NACHTRIEB on liquid sodium confirms the results of CARERI.

— F. SEITZ:

Perhaps some further information can be obtained from the angular correlation of γ-decay in solid and liquid indium. By the way, has the Kirkendall effect ever been observed in liquids?

— G. CARERI:

There are many experimental difficulties to show the Kirkendall effects in liquids Let me show a Table where the ionic conductivity and viscosity data have been recollected for alkali and silver halides. If one assumes the Einstein relation between diffusion and ionic mobility to be satisfied, this Table resembles very closely the one already shown for metals. One just wonders how these two different classes of substances can have a similar behaviour in the liquid state.

	T_m (°K)	Ionic conductivity				Viscosity	
		Crystal		Liquid			
		σ_0	E_σ	σ_0	E_σ	$\eta_0 \cdot 10^{-4}$	E_η
KCl	1 043	$2 \cdot 10^7$	53 000	6.5	2 300	4.29	7 400
NaCl	1 073	$9 \cdot 10^4$	39 600	7.4	1 580	2.11	9 100
KBr	611	$1 \cdot 10^6$	45 000	6.3	2 730	2.92	7 960
AgCl	728	$2.8 \cdot 10^3$	16 100	6.8	720	7.64	5 300
AgBr	703	$8.5 \cdot 10^3$	15 200	4.9	575	11.70	4 850

— P. G. BORDONI:

How close did you get to the melting point?

— G. CARERI:

We have published some results on indium where the diffusion near the melting point was investigated; but our technique does not seem to be the right one for this problem.

Some Remarks Concerning the Thermodynamics of Diffusion Phenomena.

G. J. HOOYMAN

Institute for Theoretical Physics, University of Utrecht

The phenomenological equations governing diffusion phenomena can be incorporated within thermodynamics of irreversible processes ([1]) which leads to relations between various diffusion coefficients. In a system of n components with velocities $\boldsymbol{v}_k$ $(k=1,\dots,n)$ we describe the diffusion with respect to some mean velocity $\boldsymbol{v}^a$

$$\boldsymbol{v}^a = \sum_k w_k \boldsymbol{v}_k \,, \tag{1}$$

the w_k being weight factors $\left(\sum w_k = 1\right)$. With N_k the molar concentrations the interdependency of the diffusion flows $\boldsymbol{J}_k^a = N_k(\boldsymbol{v}_k - \boldsymbol{v}^a)$ is given by

$$\sum_k w_k \boldsymbol{J}_k^a / N_k = 0 \,. \tag{2}$$

As feasible choices of the reference velocity $\boldsymbol{v}^a$ we mention the centre-of-mass velocity, the mean molar velocity, the mean volume velocity and the velocity of one of the components, *e.g.* the solvent in dilute solutions. ([2,3])

In thermodynamics of irreversible processes the central quantity is the entropy production σ arising from irreversible changes of the system under consideration. It is found by transforming the second law of thermodynamics with the help of the energy equation and the law of conservation of mass to a balance equation

$$\partial s_v / \partial t = -\operatorname{div} \boldsymbol{J}_s + \sigma \,, \tag{3}$$

expressing that the local change of entropy per unit volume s_v is the result of an entropy flow $\boldsymbol{J}_s$ and an entropy production σ. In the case of pure diffusion of uncharged particles (*i.e.* if we neglect external forces, temperature gradients,

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([1]) I. PRIGOGINE: *Étude thermodynamique des phénomènes irréversibles* (Paris-Liège, 1947); S. R. DE GROOT: *Thermodynamics of irreversible processes* (Amsterdam, 1951).

([2]) G. J. HOOYMAN, H. HOLTAN Jr., P. MAZUR and S. R. DE GROOT: *Physica*, **19**, 1095 (1953).

([3]) I. PRIGOGINE: *Bull. Acad. Roy. Belg.*, Cl. Sc. [5] **34**, 930 (1948).

viscosity and chemical reactions) and if we can assume the system to be in mechanical equilibrium (where the pressure is uniform) σ is given by

$$T\sigma = -\sum_{k=1}^{n} \boldsymbol{J}_k^a \cdot (\operatorname{grad} \mu_k)_{P,T} \,. \tag{4}$$

The fact that this expression is valid for arbitrary choices of the reference velocity $\boldsymbol{v}^a$ results from the condition of mechanical equilibrium according to a theorem due to PRIGOGINE [1]. $T\sigma$ is seen to be a sum of products of fluxes $\boldsymbol{J}_k^a$ and corresponding « affinities » $(\operatorname{grad} \mu_k)_{P,T}$. Since the fluxes are inter-related by (2) and the affinities by the Gibbs-Duhem relation one might eliminate one of the fluxes $\boldsymbol{J}_k^a$ and one of the chemical potentials μ_k from (4). Between the fluxes and affinities linear relationships are assumed which constitute phenomenological equations (Fick's law).

In the case of a *binary* mixture $T\sigma$ can be written as

$$T\sigma = -\boldsymbol{J}_1^a \cdot w_2^{-1} (\operatorname{grad} \mu_1)_{P,T} = -\boldsymbol{J}_1^a \cdot w_2^{-1} (\partial \mu_1 / \partial n_1)_{P,T} \operatorname{grad} n_1 \,, \tag{5}$$

where n_1 is the mole fraction N_1/N and $N = N_1 + N_2$. For an isotropic medium we can write Fick's law in the form

$$\boldsymbol{J}_1^a = -\, w_2 n_2^{-1} N D \operatorname{grad} n_1 \,, \tag{6}$$

which permits the interchange of the indexes 1 and 2 and can easily be reduced to the various forms in which Fick's law is usually stated. The diffusion coefficient D defined by (6) is independent of the w_k (and thus of the special choice of the reference velocity $\boldsymbol{v}^a$) and is quite appropriate to connect the various diffusion coefficients used by different authors [4].

For a *ternary* mixture (*) we write

$$T\sigma = -\sum_{k=1}^{2} \boldsymbol{J}_k^a \cdot \sum_{j=1}^{2} F_{kj} \operatorname{grad} N_j \,, \tag{7}$$

$$F_{kj} = \left(1 + \frac{w_k}{w_3}\right) \frac{\partial \mu_k}{\partial N_j} + \frac{w_k N_i}{w_3 N_k} \frac{\partial \mu_i}{\partial N_j} \qquad (i, k, j = 1, 2;\, i \neq k) \,. \tag{8}$$

The phenomenological equations are

$$\boldsymbol{J}_k^a = -\sum_{l=1}^{2} L_{kl}^a \{ \sum_{j=1}^{2} F_{lj} \operatorname{grad} N_j \} \equiv -\sum_{j=1}^{2} D_{kj}^a \operatorname{grad} N_j \,. \tag{9}$$

Now Onsager's theorem states that the scheme of coefficients is symmetric, *i.e.*

$$L_{12}^a = L_{21}^a \quad \text{or} \quad D_{11}^a F_{12} + D_{21}^a F_{22} = D_{12}^a F_{11} + D_{22}^a F_{21} \,, \tag{10}$$

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(4) See § 7A of the paper quoted in (2).

(*) Experimental investigation by Prof. G. CARERI of Rome.

which means that we are left with only 3 independent diffusion coefficients. The combining of (9) with the conservation law of mole numbers

$$(11) \qquad \partial N_k/\partial t = -\operatorname{div} N_k \boldsymbol{v}_k = -\operatorname{div} \boldsymbol{J}_k^a - \operatorname{div} N_k \boldsymbol{v}^a ,$$

leads to the differential equation for the diffusion (Fick's second law). In practical cases one can assume some mean velocity $\boldsymbol{v}^a$ to vanish throughout the system (*e.g.*, the volume velocity in a closed vessel (2) or the velocity of the solvent in a dilute solution). For this particular choice of the reference velocity $\boldsymbol{v}^a$ the insertion of (9) in (11) then yields for the case of one-dimensional diffusion

$$(12) \qquad \partial N_k/\partial t = D_{k1}^a \, \partial^2 N_1/\partial x^2 + D_{k2}^a \, \partial^2 N_2/\partial x^2 , \qquad (k = 1, 2)$$

if the D_{kj}^a are almost independent of the concentrations and thus of space coordinates.

INTERVENTI E DISCUSSIONI

— H. C. Longuet-Higgins:

Onsager in 1945 deduced a set of equations similar to those of Hooyman, with the minor difference that his fluxes were defined relative to the bulk velocity. Onsager's equations may therefore be more convenient for the analysis of experiments carried out in static systems.

— G. J. Hooyman:

The description of diffusion with respect to the mean volume velocity has been applied successfully, *e.g.*, in the case of sedimentation processes in ultracentrifuges where this velocity can be taken zero (cf. also (2)).

— G. Careri:

There are some serious experimental difficulties to verify the above equation for a ternary mixture. We have integrated the system of the two differential equations, and one can see how large the error will be for the D_{ik}. The experimental derivatives of the chemical potentials are also subject to great error.

Direttore responsabile: G. POLVANI Tipografia Compositori - Bologna

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